Chiral Crystallization of a Linear Two-coordinated Palladium(0) Complex Bearing Propeller-shaped Bulky Phosphine Ligands

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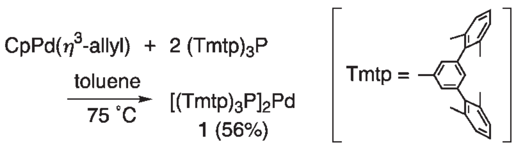
A linear bis(phosphine) palladium(0) complex with the bulky aryl substituent, tris(2,2″,6,6″-tetramethyl-*m*-terphenyl-5′-yl (Tmtp), was found to crystallize as a spontaneously resolved homochiral clathrate with toluene molecules.

Recently chiral crystallization of achiral compounds without any chiral sources is drawing attention for their potential application in asymmetric synthesis and material science.[1,2] The compounds formulated as Ar_3X have been considered to act as "molecular propellers", which in principle have two enantiomeric conformations depending on the orientation of Ar groups.[3,4] The chirality may be induced and propagated, if there exist appropriate intra- or inter-molecular interactions between Ar_3X propeller units in solid.[5] One such interaction would be non-covalent π-π stacking between the aromatic Ar groups, importance of which has been recognized in the crystal structures of various molecular assemblies.[6] Although a good number of linear molecules having two Ar_3X units at both ends are known,[3] interactions between the propeller units have not been well envisaged for them.[7,8] Most of the known Ar_3X-Y-XAr_3 compounds (e.g., X=Si, Y=O; X=Si, Ge, Y=Hg; X=Ge, Y=Cu) have *meso* forms, where aromatic rings of one Ar_3X group are twisted clockwise while the other Ar_3X group assumes a counterclockwise configuration.[3,9–12] On the other hand, the bis(phosphine) complexes of coinage metals, $[(Mes_3P)_2M](BF_4)$ (Mes = 2, 4, 6-trimethylphenly, M=Au, Ag), were reported to have a geometry where all the Mes groups are twisted to the same direction.[8] However, intramolecular and intermolecular contacts were not clearly seen in their crystal structures, which might cause the observed configuration.

We herein report synthesis of a linear two-coordinated palladium complex of triarylphosphine carrying three bulky aryls, 2,2″,6,6″-tetramethyl-*m*-terphenyl-5′-yl (denoted as Tmtp),[13] and show that crystallization from toluene/ethanol gives rise to spontaneously resolved homochiral crystals as a clathrate incorporating toluene molecules.

Bis{tris(2,2″,6,6″-tetramethyl-*m*-terphenyl-5′-yl)phosphine}-palladium, $[(Tmtp)_3P]_2Pd$ (**1**) was prepared using a procedure similar to the one reported for the synthesis of $[(^tBu)_3P]_2Pd$ and $(^tBu_2PhP)_2Pd$.[14]



Scheme 1.

A toluene solution of Cp(η^3-allyl)Pd was treated with 2 equiv of $(Tmtp)_3P$ at 75 °C for 12 h to afford **1** in 56% yield (Scheme 1). Crystallization of **1** from toluene/ethanol gave light yellow crystals, which are relatively stable in air owing to the steric protection by the bulky phosphine ligands, and the molecular structure was determined by X-ray analysis (Figure 1).[15] Being crystallized in the hexagonal *R*32 space group, the molecule has a crystallographic C_3 axis running through the P–Pd–P bond and there are three C_2 axes at Pd perpendicular to the C_3 axis. The Pd–P distance of 2.2838(9) Å falls in the range reported for linear bis(phosphine) palladium(0) complexes.[14,16] Based on the X-ray structure, the cone angle of $(Tmtp)_3P$ was estimated to be as large as 182 °.[17] Three Tmtp groups of the phosphine ligand are twisted to the same direction with the Pd–P–C(1)–C(2) torsion angle of 37.8(3) °, and the molecule is chiral. Interestingly the P–C bonds are arranged in an eclipsed conformation along the P–Pd–P bond.

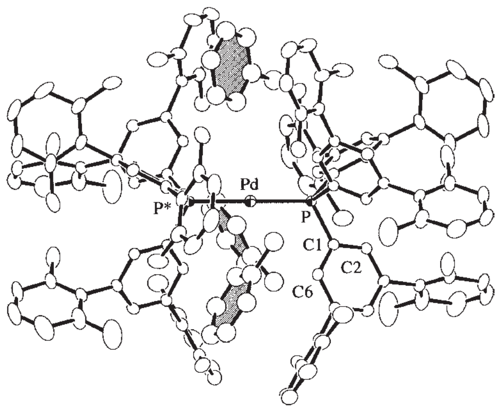


Figure 1. Molecular structure of $\mathbf{1}\cdot 3C_7H_8$, where only one set of the disordered toluene molecules are shown. Hydrogen atoms are omitted for clarity. Selected bond legths (Å) and angles (deg); Pd–P 2.2838(9), P–C(1) 1.839(2), Pd–P–C(1) 116.77(8), C(1)–P–C(1)* 101.3(1), P–C(1)–C(2), 123.7(2), P–C(1)–C(6) 117.2(2).

An important aspect of the crystal structure is that it is homochiral and the chirality seems to be induced by three toluene molecules incorporated in the complex. Each toluene molecule resides between two 2,6-dimethylphenyl groups belonging to different $(Tmtp)_3P$ ligands, and the dihedral angles between the ring-planes (~15 °) and the inter-plane distances (~3.8 Å) suggest π-π stacking.[6] Although the toluene molecules are disordered over two slightly slipped positions in a 50%/50% occupancy ratio, the above argument holds true for both of the disordered structures. The π-π interactions of the aromatic rings determine the direction and/or orientation of the Tmtp groups of two propeller-shaped phosphine ligands. It is noteworthy that agostic interaction at Pd is not observed. The shortest intramolecular non-bonded contacts of Pd occur with C(1) (3.571 Å) and

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C(6) (3.739 Å), or with an H atom on C(6) (3.2 Å). The distance between Pd and *m*-H of toluene is somewhat shorter (3.0 Å), but it is 0.3 Å and 0.5 Å longer than the shortest Pd-H distance observed in $(Ph^tBu_2P)_2Pd$[14] and $[(o\text{-Tol})_3P]_2Pd$,[9] respectively.

Another important aspect is intermolecular interactions observed in the packing diagram. As Figure 2a shows, P-Pd-P bonds line up along a hexagonal *c*-axis, and each P-Pd-P bond is translated by the crystallographic symmetry to neighboring *c*-axes with a $1/3c$ (or $-1/3c$) shift. An intermolecular CH–π interaction was observed between an *m*-H atom of 2,6-dimethylphenyl and an aromatic ring of a 2,6-dimethylphenyl group of a neighboring molecule, as shown in Figure 2b. There are two intermoelcular CH–π interactions between two molecules for each Tmtp pair, and the H(15)–Y(center of the aromatic ring) distance and C(19)–H(15)–Y angle were estimated to be 2.8 Å and 154 °, respectively. The dual CH–π interactions connect molecules in the crystal to form a chiral network, and chirality is propagated to give rise to homochiral crystals.

The rotational barrier along the P–C(1) bond appears to be low in solution. Although the crystal structure is homochiral, the *o*-H protons (i.e., 4′-*H* and 6′-*H*) of the central aromatic ring of Tmtp are all equivalent in the ^{1}H-NMR spectra in toluene-d_8 at 25 °C, the resonance of which appears as a doublet of triplet at 7.77 ppm. Likewise the *p*-H protons of 2,6-dimethylphenyl (i.e., 4-*H* and 4″-*H*) are also equivalent, appearing as a triplet signal at 6.03 ppm. These signals broaden gradually by lowering the temperature down to −60 °C, but they do not split into separated signals. The $^{31}P\{^1H\}$-NMR shows only one signal at 28.9 ppm in the temperature range of 25 °C–−60 °C. On the other hand, the *o*-C*H*$_3$ protons and the *m*-H protons of two 2,6-dimethylphenyl groups of Tmtp were observed as two sets of singlets and doublets, indicating a high rotational barrier along the C-C bond connecting aromatic rings. Both the *o*-C*H*$_3$ protons and the *m*-H protons are equivalent in the ^{1}H-NMR spectra of free $(Tmtp)_3P$. Therefore, the C-C bond rotation must be hindered by steric repulsion between two $(Tmtp)_3P$ ligands of **1**, which manifests rigidity of the molecular structure.

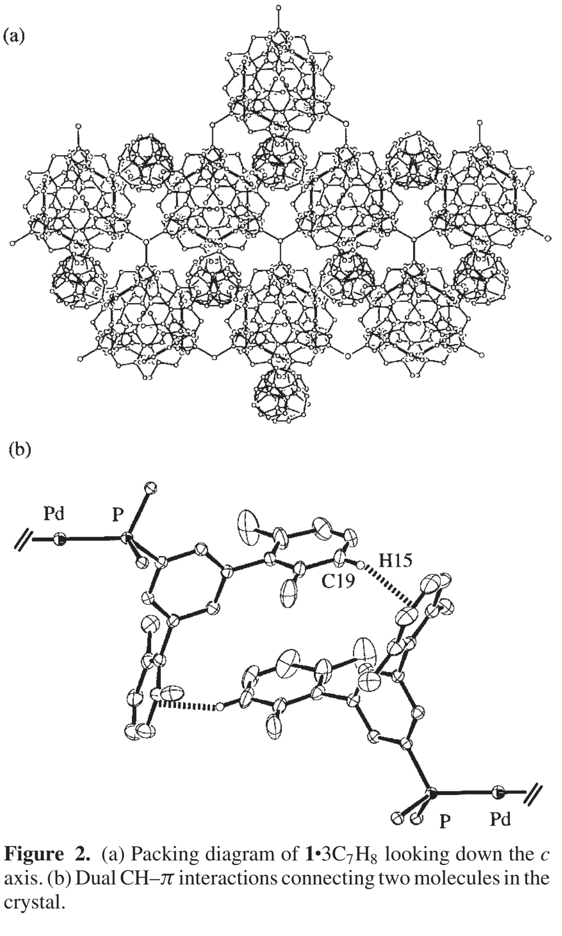

Figure 2. (a) Packing diagram of $\mathbf{1}\cdot 3C_7H_8$ looking down the *c* axis. (b) Dual CH–π interactions connecting two molecules in the crystal.

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15 Crystal data for **1**: $C_{132}H_{126}P_2Pd\cdot 3C_7H_8$, $M = 2157.22$, trigonal, *R*32, $a, b = 17.0670(8)$, $c = 40.883(2)$ Å, $V = 10313.0(9)$ Å^3, $Z = 3$, $D_{calc} = 1.042$ g/cm^3, $T = 193$ K, $R = 0.053$, $R_w = 0.065$, GOF = 0.97, 211 variables, Flack Parameter −0.044(35), 40569 reflection measured, 5291 unique ($R_{\text{int}} = 0.030$), 5218 ($I > 0.00\sigma$) observed. The data collections were made with a Rigaku-AFC7 diffractometer equipped with a MSC/ADSC Quantum1 CCD detector. The structure was solved by a teXsan package. The positions and thermal parameters for hydrogen atoms were not refined. Although the space group may be *R*3, $R\bar{3}$, *R*32, *R*3m, or $R\bar{3}$m according to the systematic absence, subsequent structure and least-squares refinement indicated the correct space group to be *R*32. Spectroscopic data: **1**, light yellow crystals, ^{1}H NMR (toluene-d_8, 500 MHz) δ2.06 (s, 36H), 2.07 (s, 36H), 6.03 (t, $J = 1.5$ Hz, 6H), 7.13 (d, $J = 8.0$ Hz, 12H), 7.14 (d, $J = 8.0$ Hz, 12H), 7.25 (t, $J = 8.0$ Hz, 12H), 7.77 (dt, $J_{H\text{-}H} = 1.5$ Hz, $J_{P\text{-}H} = 5.0$ Hz, 12H, 4′- and 6′-CH); $^{31}P\{^1H\}$ NMR (toluene-d_8, 202 MHz) δ28.86. Anal. Found: C, 84.04; H, 6.85%. Calcd for $C_{132}H_{126}P_2Pd$: C, 84.30; H, 6.75%.

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17 From the crystal structure shown in Figure 1, Pd–P distance is ca. 2.28 Å and the largest angle is estimated to 182 °. See C. A. Tolman, *Chem Rev.*, **77**, 313 (1977).