Boronic Acids: New Coupling Partners in Room-Temperature Suzuki Reactions of Alkyl Bromides. Crystallographic Characterization of an Oxidative-Addition Adduct Generated Under Remarkably Mild Conditions

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Supporting Information

I. General

Pd(OAc)₂ (Johnson Matthey), P(*t*-Bu)₂Me (Strem), KO*t*-Bu (Strem or Aldrich), 6-bromohexan-1-ol (Aldrich), 6-bromohexanoyl chloride (Avocado), phenylboronic acid (Frontier Scientific), 4-methylthiophenylboronic acid (Frontier Scientific), 4-methoxyphenylboronic acid (Frontier Scientific), 4-trifluoromethylphenylboronic acid (Frontier Scientific), 2-methylphenylboronic acid (Frontier Scientific), naphthalene-1-boronic acid (Frontier Scientific), 2,4,6-trimethylphenylboronic acid (Frontier Scientific), *trans*-1-hexen-1-ylboronic acid (Aldrich), *n*-hexylboronic acid (Avocado), pivaloyl chloride (Avocado), morpholine (Aldrich), 1-bromo-3-phenylpropane (Aldrich), and Bu₄PCl (Aldrich) were used as received. 1-Bromooctane (Avocado), (6-bromohexyloxy)-*t*-butyldimethylsilane (Aldrich), 1-bromo-2-cyclohexylethane (Aldrich), 7-bromoheptanenitrile (Aldrich), and 1-bromododecane (Avocado) were sparged with argon prior to use. *t*-Amyl alcohol (Avocado) was distilled from calcium hydride under argon.

1-Bromo-6-benzyloxyhexane,¹ 2-(10-bromodecyl)-1,3-dioxolane,² PCy₂Et,³ P(*t*-Bu)₂Et,³ [HP(*t*-Bu)₂Me]BF₄,³ and (π-allyl)PdCp⁴ were prepared according to literature procedures.

II. Preparation of Substrates

6-Bromohexyl pivalate. Under argon, 6-bromohexan-1-ol (2.74 g, 13.6 mmol, 1.0 equiv), NEt₃ (2.49 mL, 17.7 mmol, 1.3 equiv), and DMAP (41 mg, 0.27 mmol, 2%) were dissolved in dry CH₂Cl₂ (30 mL) and cooled to 0 °C. Pivaloyl chloride (2.01 mL, 16.4 mmol, 1.2 equiv) was added dropwise, leading to the formation of a white precipitate. The reaction mixture was allowed to warm to room temperature overnight, and then it was diluted with Et₂O (100 mL) and washed with water (2 × 10 mL). The aqueous phase was extracted with Et₂O (10 mL), and the combined organic layers were washed with brine (10 mL), dried over MgSO₄, filtered, and concentrated. The resulting yellow residue was purified by flash chromatography (hexanes/EtOAc 20:1), which afforded the title compound as a colorless liquid (3.29 g, 91%).

¹H NMR (CDCl₃, 300 MHz): δ 4.03 (t, *J* = 6.5 Hz, 2H), 3.38 (t, *J* = 6.8 Hz, 2H), 1.85 (tt, *J* = 6.9, 6.7 Hz, 2H), 1.62 (tt, *J* = 6.9, 6.7 Hz, 2H), 1.50-1.32 (m, 4H), 1.17 (s, 9H). ¹³C NMR (CDCl₃, 75 MHz): δ 178.4, 64.3, 38.9, 33.9, 32.8, 28.7, 28.0, 27.4, 25.4. IR (thin film): 2937, 2869, 1729, 1481, 1461, 1398, 1366, 1285, 1159, 1043, 1006, 771, 723 cm⁻¹. HRMS (ESI): Calcd for C₁₁H₂₁O₂BrNa (M+Na)⁺: 287.0617. Found: 287.0625.

6-Bromo-1-(morpholin-4-yl)-hexan-1-one [134413-96-0]. Under argon, morpholine (2.20 mL, 25.0 mmol, 1.0 equiv), NEt₃ (5.40 mL, 37.5 mmol, 1.5 equiv), and DMAP (76 mg, 0.50 mmol, 2%) were dissolved in dry CH₂Cl₂ (50 mL) and cooled to 0 °C. A solution of 6-bromohexanoyl chloride (5.34 g, 25.0 mmol, 1.0 equiv) in dry CH₂Cl₂ (10 mL) was added dropwise. After stirring for 2 hours at room temperature, the reaction mixture was diluted with Et₂O (300 mL) and washed successively with 1 M HCl (30 mL), saturated aqueous NaHCO₃ (30 mL), and water (10 mL). The organic phase was dried over MgSO₄, filtered, and concentrated, and the resulting residue was purified by flash chromatography (hexanes/EtOAc 1:4), which afforded the title compound as a colorless oil (6.30 g, 95%).

¹H NMR (CDCl₃, 300 MHz): δ 3.61-3.54 (m, 4H), 3.54-3.48 (m, 2H), 3.38 (m, 2H), 3.33 (t, *J* = 6.7 Hz, 2H), 2.25 (t, *J* = 7.4 Hz, 2H), 1.80 (m, 2H), 1.58 (m, 2H), 1.47-1.35 (m, 2H).

^{13}C NMR (CDCl_3 , 75 MHz): δ 171.0, 66.8, 66.6, 45.9, 41.8, 33.8, 32.8, 32.5, 27.9, 24.3. IR (thin film): 3488, 2931, 2857, 1643, 1432, 1300, 1273, 1229, 1115, 1032, 966, 849, 732, 640, 566 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{10}\text{H}_{18}\text{BrNO}_2\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$: 286.0413. Found: 286.0417.

III. Suzuki Cross-Couplings (Table 2)

Cross Coupling Procedure A (with $P(t\text{-Bu})_2\text{Me}$). In a glove box, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.0500 mmol, 5%), the boronic acid (1.50 mmol, 1.50 equiv), $\text{KO}t\text{-Bu}$ (336 mg, 3.00 mmol, 3.00 equiv), and $P(t\text{-Bu})_2\text{Me}$ (20 μL , 0.10 mmol, 10%) were placed in a screw-cap vial equipped with a stir bar. *t*-Amyl alcohol (5.0 mL) and then the alkyl bromide (1.00 mmol, 1.00 equiv) were added, and the resulting heterogeneous reaction mixture was stirred vigorously for 24 hours at room temperature. The reaction mixture was then poured into Et_2O (30 mL), filtered through a short pad of silica gel with copious washings (Et_2O or EtOAc , ~100 mL), concentrated, and purified by column chromatography.

Cross-Coupling Procedure B (with $[\text{HP}(t\text{-Bu})_2\text{Me}]\text{BF}_4$). In air, $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.0500 mmol, 5%), $[\text{HP}(t\text{-Bu})_2\text{Me}]\text{BF}_4$ (25 mg, 0.10 mmol, 10%), the boronic acid (1.50 mmol, 1.50 equiv), and $\text{KO}t\text{-Bu}$ (336 mg, 3.00 mmol, 3.00 equiv) were placed in a vial equipped with a stir bar. The vial was sealed with a septum screw-cap, and then it was evacuated and filled with argon (three cycles). *t*-Amyl alcohol (5.0 mL) and then the alkyl bromide (1.00 mmol, 1.00 equiv) were added, and the resulting heterogeneous reaction mixture was stirred vigorously for 24 hours at room temperature. The reaction mixture was then poured into Et_2O (30 mL), filtered through a short pad of silica gel with copious washings (Et_2O or EtOAc , ~100 mL), concentrated, and purified by column chromatography.

1-Phenyloctane [2189-60-8] (Table 2, entry 1). Solvent for chromatography: hexanes. Colorless liquid (Procedure A: 165 mg, 87%; Procedure B: 172 mg, 90%), identical (^1H NMR, ^{13}C NMR, and GC) to an authentic sample (Aldrich).

6-(4-(Methylthio)phenyl)hexyl pivalate (Table 2, entry 2). Solvent for chromatography: hexanes/ EtOAc 20:1. Yellow oil (Procedure A: 210 mg, 68%; Procedure B: 205 mg, 66%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.20 (dt, $J = 8.3$ Hz, 1.9 Hz, 2H), 7.10 (dt, $J = 8.3$ Hz, 1.9

Hz, 2H), 4.06 (t, $J = 6.6$ Hz, 2H), 2.59 (t, $J = 7.6$ Hz, 2H), 2.49 (s, 3H), 1.63 (m, 4H), 1.39 (m, 4H), 1.22 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 178.6, 139.8, 135.1, 129.0, 127.1, 64.6, 39.0, 35.5, 31.6, 29.1, 28.8, 27.5, 26.1, 16.7. IR (thin film): 2932, 2857, 1727, 1495, 1480, 1285, 1156, 1095, 968, 805, 732 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 331.1702. Found 331.1700.

1-Benzyloxy-6-(4-methoxyphenyl)hexane (Table 2, entry 3). Solvent for chromatography: hexanes/EtOAc 30:1. Colorless oil (Procedure A: 253 mg, 85%; Procedure B: 250 mg, 84%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.43-7.28 (m, 5H), 7.14 (dt, $J = 8.8$ Hz, 2.5 Hz, 2H), 6.87 (dt, $J = 8.8$ Hz, 2.5 Hz, 2H), 4.55 (s, 2H), 3.83 (s, 3H), 3.52 (t, $J = 6.5$ Hz, 2H), 2.61 (t, $J = 7.6$ Hz, 2H), 1.68 (m, 4H), 1.44 (m, 4H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 157.5, 138.7, 134.9, 129.3, 128.4, 127.7, 127.5, 113.7, 73.0, 70.6, 55.4, 35.2, 31.9, 30.0, 29.3, 26.3. IR (thin film): 2932, 2856, 1612, 1513, 1454, 1246, 1177, 1115, 1037, 828, 735, 698 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2$ (M^+): 298.1927. Found 298.1939.

1-(*t*-Butyldimethylsiloxy)-6-(4-(trifluoromethyl)phenyl)hexane (Table 2, entry 4). Solvent for chromatography: hexanes/EtOAc 75:1 to 30:1. Colorless liquid (Procedure A: 228 mg, 63%; Procedure B: 242 mg, 67%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.54 (d, $J = 7.8$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), 3.64 (t, $J = 6.5$ Hz, 2H), 2.69 (t, $J = 7.7$ Hz, 2H), 1.76-1.61 (m, 2H), 1.60-1.48 (m, 2H), 1.47-1.32 (m, 4H), 0.94 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 147.0, 128.8, 128.1 (q , $^2J_{\text{C-F}} = 32$ Hz), 125.3 (q , $^3J_{\text{C-F}} = 3.8$ Hz), 124.5 (q , $^1J_{\text{C-F}} = 125$ Hz), 63.4, 36.0, 33.0, 31.5, 29.3, 26.3, 26.0, 18.7, -4.9. IR (thin film): 2932, 2857, 1619, 1472, 1464, 1326, 1256, 1165, 1126, 1068, 836, 776 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{31}\text{F}_3\text{OSiNa}$ ($\text{M}+\text{Na}$) $^+$: 383.1988. Found: 383.1991.

6-(2-Methylphenyl)hexanoic acid, morpholine amide (Table 2, entry 5). Solvent for chromatography: hexanes/EtOAc 1:3 to 1:4. Colorless oil (Procedure A: 195 mg, 71%; Procedure B: 210 mg, 76%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.18-7.06 (m, 4H), 3.67 (m, 6H), 3.46 (m, 2H), 2.63 (t, $J = 7.7$ Hz, 2H), 2.34 (t, $J = 7.4$ Hz, 2H), 2.32 (s, 3H), 1.71 (quint, $J = 7.7$ Hz, 2H), 1.63 (quint,

$J = 7.7$ Hz, 2H), 1.52-1.39 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 171.6, 140.7, 135.8, 130.1, 128.8, 125.85, 128.81, 67.1, 66.8, 46.2, 42.0, 33.3, 33.2, 30.2, 29.7, 25.4, 19.6. IR (thin film): 3492, 2929, 2857, 2240, 1643, 1432, 1272, 1230, 1116, 1033, 963, 912, 845, 741 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 298.1778. Found: 298.1773.

2-(10-(1-Naphthyl)decyl)-1,3-dioxolane (Table 2, entry 6). Solvent for chromatography: hexanes/EtOAc 15:1. Colorless oil (Procedure A: 330 mg, 97%; Procedure B: 318 mg, 93%).

^1H NMR (CDCl_3 , 300 MHz): δ 8.10 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.89 (dd, $J = 7.7, 1.9$ Hz, 1H), 7.75 (d, $J = 8.3$ Hz, 1H), 7.60-7.33 (m, 4H), 4.90 (t, $J = 4.8$ Hz, 1H), 4.01 (m, 2H), 3.89 (m, 2H), 3.12 (t, $J = 7.8$ Hz, 2H), 1.90-1.68 (m, 4H), 1.57-1.28 (m, 14H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 139.0, 133.9, 131.9, 128.8, 126.4, 125.9, 125.65, 125.57, 125.4, 124.0, 104.8, 65.0, 34.2, 33.4, 31.1, 30.1, 29.9, 29.8 (4 coincident resonances), 24.4. IR (thin film): 3045, 2926, 2854, 1597, 1510, 1466, 1397, 1141, 1035, 944, 797, 778, 732 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{32}\text{O}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 363.2295. Found: 363.2300.

1-(2-Cyclohexylethyl)-2,4,6-trimethylbenzene (Table 2, entry 7). Solvent for chromatography: hexanes. Colorless liquid (Procedure A: 206 mg, 89%; Procedure B: 210 mg, 91%).

^1H NMR (CDCl_3 , 300 MHz): δ 6.92 (s, 2H), 2.68 (m, 2H), 2.39 (s, 6H), 2.35 (s, 2H), 2.02-1.72 (m, 5H), 1.54-1.23 (m, 7H), 1.20-1.00 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 136.9, 135.8, 134.7, 128.9, 38.7, 37.2, 33.5, 27.1, 27.0, 26.7, 21.1, 19.9. IR (thin film): 3002, 2922, 2851, 1614, 1485, 1448, 1376, 1031, 1012, 850, 589 cm^{-1} . HRMS (EI): Calcd for $\text{C}_{17}\text{H}_{26}$ (M^+): 230.2029. Found 230.2030.

(E)-Tridec-8-enenitrile (Table 2, entry 8). Solvent for chromatography: hexanes/EtOAc 20:1. Colorless liquid (Procedure A: 165 mg, 85%; Procedure B: 168 mg, 87%).

^1H NMR (CDCl_3 , 300 MHz): δ 5.38 (m, 2H), 2.34 (t, $J = 7.0$ Hz, 2H), 1.98 (m, 4H), 1.66 (quint, $J = 7.0$ Hz, 2H), 1.52-1.24 (m, 10H), 0.90 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 130.7, 129.8, 119.9, 32.6, 32.5, 32.0, 29.4, 28.7, 28.4, 25.6, 22.4, 17.3, 14.2. IR (thin film): 2928, 2856, 2247, 1465, 1378, 969, 727 cm^{-1} . HRMS (ESI): Calcd for $\text{C}_{13}\text{H}_{23}\text{NNa}$

(M+Na)⁺: 216.1723. Found: 216.1725.

***n*-Octadecane [593-45-3] (Table 2, entry 9).** Solvent for chromatography: hexanes. White solid (Procedure A: 169 mg, 66%; Procedure B: 158 mg, 62%), identical (¹H NMR, ¹³C NMR, GC, and mp) to an authentic sample (Alfa Aesar).

IV. Study of Oxidative Addition

Preparation of Pd(P(*t*-Bu)₂Me)₂. The procedure of Yoshida and Otsuka,⁵ which has been used to prepare bis(phosphine)palladium(0) complexes with other bulky trialkylphosphines, was employed: P(*t*-Bu)₂Me (570 mg, 3.54 mmol) was added to a stirred solution of (π -allyl)PdCp (340 mg, 1.60 mmol) in toluene (15 mL) in a Schlenk tube under nitrogen. The vessel was closed and heated to 75 °C for 3 h. The reaction mixture was then cooled to room temperature, the solvent was removed under reduced pressure, and the dark residue was dried under high vacuum for 1 h. Attempts to triturate or recrystallize the resulting solid were unsuccessful due to its high solubility in a wide range of organic solvents, including MeOH. Because the palladium complex was pure by ¹H, ¹³C, and ³¹P NMR spectroscopy, it was used without additional purification.

¹H NMR (C₆D₆, 300 MHz): δ 1.28 (br s, 36H), 1.07 (s, 6H). ¹³C NMR (C₆D₆, 75 MHz): δ 33.4, 30.6, 7.7. ³¹P NMR (C₆D₆, 121 MHz): δ 41.0.

Preparation of *trans*-Pd(P(*t*-Bu)₂Me)₂(Br)CH₂CH₂CH₂Ph (1; eq 2). Pd(P(*t*-Bu)₂Me)₂ (1.41 mmol) was prepared as described above from (π -allyl)PdCp (300 mg, 1.41 mmol) and P(*t*-Bu)₂Me (459 mg, 2.86 mmol) in toluene (4 mL). Under an atmosphere of nitrogen, this Pd(P(*t*-Bu)₂Me)₂ was dissolved in Et₂O and cooled to 0 °C. 1-Bromo-3-phenylpropane (459 μ L, 3.02 mmol) was added, and the reaction was stirred at 0 °C for 41 h. The resulting off-white precipitate was filtered under nitrogen, washed with Et₂O, and dried under vacuum to provide the title compound as a fine, pale-yellow powder (830 mg, 94%). The solid was stored under nitrogen at -35 °C (the complex is not stable in solution). X-ray quality crystals were prepared by careful dissolution of the complex in THF at 30 °C, followed by the addition of Et₂O and crystallization at 0 °C.

¹H NMR (THF-*d*₈, 500 MHz): δ 7.22-7.19 (m, 2H), 7.13-7.09 (m, 3H), 2.54 (t, *J* = 7.3 Hz, 2H), 1.70 (m, 2H), 1.44 (br apparent t, *J* = 5.8 Hz, 36H), 1.29-1.25 (m, 2H), 1.16 (br s, 6H). ¹³C NMR (THF-*d*₈, 125 MHz): δ 143.4, 129.5, 129.1, 126.4, 41.0 (br), 36.6 (br), 34.8, 31.0

(C(CH₃)₃), 19.6, 2.2 (br). ³¹P NMR (THF-*d*₈, 203 MHz): δ 27.6.

Reaction of *trans*-Pd(P(*t*-Bu)₂Me)₂(Br)CH₂CH₂CH₂Ph (1) with *o*-tolylboronic acid/KO*t*-Bu (eq 3). In a glove box, a suspension of *trans*-Pd(P(*t*-Bu)₂Me)₂(Br)CH₂CH₂CH₂Ph (188 mg, 0.300 mmol) in *t*-amyl alcohol (1 mL) was added to a solution of *o*-tolylboronic acid (45 mg, 0.33 mmol) and KO*t*-Bu (74 mg, 0.66 mmol) in *t*-amyl alcohol (5 mL). The resulting suspension was stirred vigorously at room temperature for 16 h. An internal standard for ³¹P NMR (Bu₄PCl) was then added, and the mixture was analyzed by ³¹P NMR, which showed Pd(P(*t*-Bu)₂Me)₂ (δ 41.2) to be the only phosphorus-containing compound that was present (89% yield vs. the internal standard). The reaction mixture was diluted with Et₂O, filtered through silica gel with copious washings, and concentrated. Flash chromatography (hexanes) provided 1-(2-methylphenyl)-3-phenylpropane [1520-39-4] as a colorless liquid (58 mg, 92%).

A second run furnished the product in 95% yield.

¹H NMR (CDCl₃, 300 MHz): δ 7.36-7.10 (m, 9H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 2.02-1.91 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz): δ 142.3, 140.5, 136.0, 130.2, 128.8, 128.5, 128.4, 125.97, 125.96, 125.86, 36.1, 33.2, 32.0, 19.6. IR (thin film): 3062, 3025, 2936, 2861, 1603, 1495, 1453, 745, 699 cm⁻¹. HRMS (EI): Calcd for C₁₆H₁₈ (M⁺): 210.1403. Found 210.1399.

V. X-Ray Crystal Structure of 1

A light-yellow block of dimensions $0.39 \times 0.33 \times 0.16 \text{ mm}^3$ was mounted under STP and transferred to a Bruker AXS/CCD three-circle diffractometer (χ fixed at 54.78°) equipped with a cold stream of N_2 gas. An initial unit cell was determined by harvesting reflections $I > 20 \sigma(I)$ from 45×10 -s frames of 0.30° ω scan data with monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The cell thus determined was orthorhombic.

A hemisphere of data was then collected using ω scans of 0.30° and 10-s frames. The raw data frames were integrated using the Bruker program SAINT+ for NT version 6.01. The data that were collected (22703 total reflections, 4332 unique, $R_{\text{int}} = 0.0660$) had the following Miller index ranges: -10 to 12 in h , -18 to 20 in k , and -32 to 32 in l . The data were corrected for Lorentz and polarization effects. An SADABS absorption correction was applied with $\mu = 2.06 \text{ mm}^{-1}$.

All aspects of the solution and refinement were handled by SHELXTL Windows NT version 5.10. The structure was solved by direct methods in the orthorhombic space group $Pbca$, $a = 11.1382(7) \text{ \AA}$; $b = 18.3329(11) \text{ \AA}$; $c = 29.5216(18) \text{ \AA}$; $\alpha = 90^\circ$; $\beta = 90^\circ$; $\gamma = 90^\circ$, and refined using standard difference Fourier techniques. Final, full-matrix least-squares refinement (4332 data for 294 parameters) on F^2 yielded residuals of R_1 and wR_2 of 0.0613 and 0.1410 for data $I > 2\sigma(I)$, and 0.0631 and 0.1420, respectively, for all data. During the final refinement, all non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in calculated positions and refined isotropically on a riding model. No secondary extinction coefficient was used in the refinement. Residual electron density amounted to a maximum of $0.994 e/\text{\AA}^3$ and a minimum of $-0.982 e/\text{\AA}^3$.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC# 192705. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Tables 1-6 provide the full crystallographic data for the X-ray structure.

Table 1. Crystal data and structure refinement for 02152MNS.

Identification code	02152mns	
Empirical formula	C ₂₇ H ₅₃ Br P ₂ Pd	
Formula weight	625.94	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.1382(7) Å	$\alpha = 90^\circ$.
	b = 18.3329(11) Å	$\beta = 90^\circ$.
	c = 29.5216(18) Å	$\gamma = 90^\circ$.
Volume	6028.2(6) Å ³	
Z	8	
Density (calculated)	1.379 Mg/m ³	
Absorption coefficient	2.060 mm ⁻¹	
F(000)	2608	
Crystal size	0.39 x 0.33 x 0.16 mm ³	
Theta range for data collection	2.25 to 23.27°.	
Index ranges	-10 ≤ h ≤ 12, -18 ≤ k ≤ 20, -32 ≤ l ≤ 32	
Reflections collected	22703	
Independent reflections	4332 [R(int) = 0.0660]	
Completeness to theta = 23.27°	99.8 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4332 / 0 / 294	
Goodness-of-fit on F ²	1.287	
Final R indices [I > 2σ(I)]	R1 = 0.0613, wR2 = 0.1410	
R indices (all data)	R1 = 0.0631, wR2 = 0.1420	
Largest diff. peak and hole	0.994 and -0.982 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02152MNS. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Pd(1)	3508(1)	852(1)	6088(1)	23(1)
Br(1)	2467(1)	2098(1)	6187(1)	39(1)
P(1)	5255(2)	1400(1)	5768(1)	26(1)
P(2)	1798(2)	205(1)	6357(1)	24(1)
C(1)	4324(6)	-155(3)	6001(2)	28(2)
C(2)	5013(6)	-393(3)	6420(2)	27(2)
C(3)	5591(7)	-1141(4)	6358(2)	36(2)
C(4)	6176(6)	-1429(3)	6782(2)	28(2)
C(5)	5631(7)	-1965(4)	7036(3)	38(2)
C(6)	6159(8)	-2235(4)	7429(3)	44(2)
C(7)	7241(7)	-1974(4)	7570(2)	38(2)
C(8)	7795(7)	-1441(4)	7319(3)	40(2)
C(9)	7265(6)	-1175(4)	6935(2)	35(2)
C(10)	6168(7)	1985(4)	6166(2)	33(2)
C(11)	5396(8)	2576(5)	6382(3)	59(3)
C(12)	6590(9)	1491(5)	6545(3)	65(3)
C(13)	7268(8)	2342(6)	5939(3)	61(3)
C(14)	4919(7)	1883(4)	5216(2)	35(2)
C(15)	4468(8)	2668(4)	5286(3)	47(2)
C(16)	3897(8)	1444(5)	4998(3)	49(2)
C(17)	5979(8)	1912(5)	4889(3)	53(2)
C(18)	6409(7)	752(4)	5573(3)	43(2)
C(19)	618(7)	169(4)	5896(3)	40(2)
C(20)	-553(7)	-219(5)	6050(4)	59(3)
C(21)	300(8)	913(4)	5724(3)	49(2)
C(22)	1205(9)	-272(5)	5511(3)	60(2)
C(23)	1178(7)	522(4)	6920(2)	37(2)
C(24)	482(8)	-64(5)	7180(3)	51(2)
C(25)	349(9)	1181(5)	6882(3)	57(2)
C(26)	2281(8)	723(5)	7197(3)	51(2)
C(27)	2007(6)	-761(4)	6486(3)	36(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for 02152MNS.

Pd(1)-C(1)	2.074(6)
Pd(1)-P(2)	2.3799(18)
Pd(1)-P(1)	2.3855(18)
Pd(1)-Br(1)	2.5783(9)
P(1)-C(18)	1.843(7)
P(1)-C(10)	1.888(7)
P(1)-C(14)	1.891(7)
P(2)-C(27)	1.826(7)
P(2)-C(23)	1.891(7)
P(2)-C(19)	1.894(7)
C(1)-C(2)	1.520(9)
C(2)-C(3)	1.526(9)
C(3)-C(4)	1.505(9)
C(4)-C(9)	1.376(10)
C(4)-C(5)	1.379(10)
C(5)-C(6)	1.391(11)
C(6)-C(7)	1.361(11)
C(7)-C(8)	1.374(11)
C(8)-C(9)	1.369(11)
C(10)-C(12)	1.515(11)
C(10)-C(11)	1.521(12)
C(10)-C(13)	1.542(11)
C(14)-C(17)	1.526(11)
C(14)-C(16)	1.536(11)
C(14)-C(15)	1.539(11)
C(19)-C(21)	1.499(11)
C(19)-C(22)	1.541(12)
C(19)-C(20)	1.553(11)
C(23)-C(26)	1.521(12)
C(23)-C(25)	1.525(11)
C(23)-C(24)	1.530(11)
C(1)-Pd(1)-P(2)	87.0(2)
C(1)-Pd(1)-P(1)	88.2(2)
P(2)-Pd(1)-P(1)	174.28(6)
C(1)-Pd(1)-Br(1)	179.1(2)
P(2)-Pd(1)-Br(1)	92.54(5)
P(1)-Pd(1)-Br(1)	92.18(5)

C(18)-P(1)-C(10)	100.7(4)
C(18)-P(1)-C(14)	99.8(4)
C(10)-P(1)-C(14)	112.2(3)
C(18)-P(1)-Pd(1)	114.9(3)
C(10)-P(1)-Pd(1)	115.6(2)
C(14)-P(1)-Pd(1)	112.1(2)
C(27)-P(2)-C(23)	99.3(3)
C(27)-P(2)-C(19)	101.7(3)
C(23)-P(2)-C(19)	112.9(4)
C(27)-P(2)-Pd(1)	116.8(2)
C(23)-P(2)-Pd(1)	115.7(2)
C(19)-P(2)-Pd(1)	109.4(3)
C(2)-C(1)-Pd(1)	112.1(4)
C(1)-C(2)-C(3)	111.9(5)
C(4)-C(3)-C(2)	113.4(6)
C(9)-C(4)-C(5)	116.7(6)
C(9)-C(4)-C(3)	122.4(6)
C(5)-C(4)-C(3)	120.9(7)
C(4)-C(5)-C(6)	121.5(7)
C(7)-C(6)-C(5)	120.3(7)
C(6)-C(7)-C(8)	118.8(7)
C(9)-C(8)-C(7)	120.5(7)
C(8)-C(9)-C(4)	122.1(7)
C(12)-C(10)-C(11)	107.0(7)
C(12)-C(10)-C(13)	109.1(7)
C(11)-C(10)-C(13)	109.2(7)
C(12)-C(10)-P(1)	106.7(5)
C(11)-C(10)-P(1)	111.1(5)
C(13)-C(10)-P(1)	113.4(5)
C(17)-C(14)-C(16)	109.1(6)
C(17)-C(14)-C(15)	107.7(6)
C(16)-C(14)-C(15)	107.7(7)
C(17)-C(14)-P(1)	114.1(6)
C(16)-C(14)-P(1)	105.2(5)
C(15)-C(14)-P(1)	112.7(5)
C(21)-C(19)-C(22)	109.1(7)
C(21)-C(19)-C(20)	108.5(7)
C(22)-C(19)-C(20)	109.4(7)
C(21)-C(19)-P(2)	112.1(5)

C(22)-C(19)-P(2)	104.7(5)
C(20)-C(19)-P(2)	113.0(6)
C(26)-C(23)-C(25)	109.7(7)
C(26)-C(23)-C(24)	108.1(7)
C(25)-C(23)-C(24)	106.6(6)
C(26)-C(23)-P(2)	104.5(5)
C(25)-C(23)-P(2)	113.6(5)
C(24)-C(23)-P(2)	114.2(5)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02152MNS. The anisotropic displacement factor exponent takes the form: $-2_{-}^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	25(1)	21(1)	22(1)	0(1)	-1(1)	1(1)
Br(1)	42(1)	24(1)	52(1)	-1(1)	8(1)	4(1)
P(1)	25(1)	26(1)	26(1)	-1(1)	0(1)	-2(1)
P(2)	22(1)	24(1)	27(1)	3(1)	0(1)	1(1)
C(1)	35(4)	22(3)	27(3)	0(3)	-1(3)	5(3)
C(2)	28(4)	21(3)	33(4)	-1(3)	-1(3)	7(3)
C(3)	48(4)	27(4)	34(4)	0(3)	-3(4)	10(3)
C(4)	33(4)	22(3)	28(3)	-1(3)	4(3)	12(3)
C(5)	38(4)	32(4)	45(4)	-5(3)	2(4)	2(3)
C(6)	57(5)	36(4)	39(4)	7(3)	11(4)	-2(4)
C(7)	53(5)	33(4)	29(4)	-1(3)	-4(3)	11(4)
C(8)	33(4)	43(4)	43(4)	-2(4)	1(3)	7(4)
C(9)	31(4)	30(4)	43(4)	3(3)	7(3)	4(3)
C(10)	35(4)	35(4)	28(4)	-4(3)	-6(3)	-7(3)
C(11)	60(6)	63(6)	54(5)	-28(5)	-7(5)	-25(5)
C(12)	70(6)	65(6)	59(6)	4(5)	-32(5)	-14(5)
C(13)	43(5)	76(7)	64(6)	-16(5)	11(4)	-33(5)
C(14)	45(4)	33(4)	28(4)	5(3)	0(3)	-9(3)
C(15)	61(5)	40(5)	40(4)	16(4)	0(4)	5(4)
C(16)	53(5)	68(6)	27(4)	1(4)	-6(4)	-13(5)
C(17)	58(5)	62(6)	38(4)	4(4)	14(4)	-3(5)
C(18)	34(4)	37(4)	58(5)	0(4)	8(4)	1(3)
C(19)	38(4)	37(4)	45(4)	5(3)	-13(4)	-1(3)
C(20)	34(5)	49(5)	93(7)	18(5)	-18(5)	-15(4)
C(21)	46(5)	50(5)	53(5)	15(4)	-21(4)	0(4)
C(22)	64(6)	61(6)	55(5)	-15(5)	-23(5)	0(5)
C(23)	41(4)	36(4)	36(4)	-1(3)	11(3)	1(3)
C(24)	51(5)	53(5)	49(5)	17(4)	17(4)	8(4)
C(25)	71(6)	47(5)	52(5)	-1(4)	28(5)	19(5)
C(26)	59(5)	66(6)	28(4)	-9(4)	7(4)	-2(5)
C(27)	27(4)	28(4)	53(5)	9(3)	3(3)	2(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 02152MNS.

	x	y	z	U(eq)
H(1A)	3703	-524	5930	33
H(1B)	4883	-129	5741	33
H(2A)	4458	-410	6682	33
H(2B)	5645	-29	6488	33
H(3A)	4969	-1491	6258	43
H(3B)	6203	-1108	6116	43
H(5)	4879	-2155	6942	46
H(6)	5763	-2602	7600	52
H(7)	7606	-2158	7838	46
H(8)	8551	-1255	7413	48
H(9)	7662	-803	6768	42
H(11A)	4679	2354	6516	89
H(11B)	5155	2929	6150	89
H(11C)	5858	2825	6618	89
H(12A)	6953	1786	6786	97
H(12B)	7187	1147	6427	97
H(12C)	5905	1220	6668	97
H(13A)	7747	2595	6168	92
H(13B)	6997	2692	5710	92
H(13C)	7758	1964	5794	92
H(15A)	5117	2967	5413	70
H(15B)	3787	2666	5496	70
H(15C)	4215	2872	4995	70
H(16A)	3207	1431	5204	74
H(16B)	4171	945	4938	74
H(16C)	3660	1676	4712	74
H(17A)	5742	2175	4614	79
H(17B)	6223	1415	4810	79
H(17C)	6652	2166	5033	79
H(18A)	7129	1021	5481	64
H(18B)	6100	474	5315	64
H(18C)	6612	417	5820	64
H(20A)	-929	62	6294	88

H(20B)	-362	-710	6158	88
H(20C)	-1108	-252	5793	88
H(21A)	1002	1131	5576	74
H(21B)	47	1222	5977	74
H(21C)	-357	873	5504	74
H(22A)	691	-256	5242	90
H(22B)	1307	-780	5608	90
H(22C)	1991	-62	5439	90
H(24A)	1019	-470	7252	77
H(24B)	-184	-241	6992	77
H(24C)	163	145	7461	77
H(25A)	184	1374	7185	85
H(25B)	-406	1034	6739	85
H(25C)	737	1558	6698	85
H(26A)	2723	1113	7044	77
H(26B)	2801	294	7228	77
H(26C)	2032	890	7498	77
H(27A)	2502	-811	6758	54
H(27B)	2407	-1000	6230	54
H(27C)	1223	-989	6537	54

Table 6. Torsion angles [°] for 02152MNS.

C(1)-Pd(1)-P(1)-C(18)	3.1(4)
P(2)-Pd(1)-P(1)-C(18)	-30.5(7)
Br(1)-Pd(1)-P(1)-C(18)	-176.0(3)
C(1)-Pd(1)-P(1)-C(10)	-113.5(3)
P(2)-Pd(1)-P(1)-C(10)	-147.1(6)
Br(1)-Pd(1)-P(1)-C(10)	67.3(3)
C(1)-Pd(1)-P(1)-C(14)	116.2(3)
P(2)-Pd(1)-P(1)-C(14)	82.6(7)
Br(1)-Pd(1)-P(1)-C(14)	-63.0(3)
C(1)-Pd(1)-P(2)-C(27)	12.4(3)
P(1)-Pd(1)-P(2)-C(27)	46.1(7)
Br(1)-Pd(1)-P(2)-C(27)	-168.3(3)
C(1)-Pd(1)-P(2)-C(23)	128.8(3)
P(1)-Pd(1)-P(2)-C(23)	162.5(6)
Br(1)-Pd(1)-P(2)-C(23)	-52.0(3)
C(1)-Pd(1)-P(2)-C(19)	-102.4(3)
P(1)-Pd(1)-P(2)-C(19)	-68.7(7)
Br(1)-Pd(1)-P(2)-C(19)	76.8(3)
P(2)-Pd(1)-C(1)-C(2)	-90.5(5)
P(1)-Pd(1)-C(1)-C(2)	92.7(5)
Br(1)-Pd(1)-C(1)-C(2)	-152(13)
Pd(1)-C(1)-C(2)-C(3)	178.9(5)
C(1)-C(2)-C(3)-C(4)	-174.2(6)
C(2)-C(3)-C(4)-C(9)	-76.2(9)
C(2)-C(3)-C(4)-C(5)	103.6(8)
C(9)-C(4)-C(5)-C(6)	0.1(10)
C(3)-C(4)-C(5)-C(6)	-179.8(7)
C(4)-C(5)-C(6)-C(7)	-0.4(11)
C(5)-C(6)-C(7)-C(8)	0.2(11)
C(6)-C(7)-C(8)-C(9)	0.3(11)
C(7)-C(8)-C(9)-C(4)	-0.6(11)
C(5)-C(4)-C(9)-C(8)	0.4(10)
C(3)-C(4)-C(9)-C(8)	-179.7(7)
C(18)-P(1)-C(10)-C(12)	-63.1(6)
C(14)-P(1)-C(10)-C(12)	-168.5(6)
Pd(1)-P(1)-C(10)-C(12)	61.3(6)
C(18)-P(1)-C(10)-C(11)	-179.5(6)
C(14)-P(1)-C(10)-C(11)	75.2(6)
Pd(1)-P(1)-C(10)-C(11)	-55.1(6)
C(18)-P(1)-C(10)-C(13)	57.1(7)
C(14)-P(1)-C(10)-C(13)	-48.3(7)

Pd(1)-P(1)-C(10)-C(13)	-178.5(5)
C(18)-P(1)-C(14)-C(17)	-29.3(6)
C(10)-P(1)-C(14)-C(17)	76.6(6)
Pd(1)-P(1)-C(14)-C(17)	-151.4(5)
C(18)-P(1)-C(14)-C(16)	90.2(6)
C(10)-P(1)-C(14)-C(16)	-163.9(5)
Pd(1)-P(1)-C(14)-C(16)	-31.9(6)
C(18)-P(1)-C(14)-C(15)	-152.6(6)
C(10)-P(1)-C(14)-C(15)	-46.8(7)
Pd(1)-P(1)-C(14)-C(15)	85.2(5)
C(27)-P(2)-C(19)-C(21)	-179.0(6)
C(23)-P(2)-C(19)-C(21)	75.5(7)
Pd(1)-P(2)-C(19)-C(21)	-54.8(6)
C(27)-P(2)-C(19)-C(22)	-60.8(6)
C(23)-P(2)-C(19)-C(22)	-166.3(5)
Pd(1)-P(2)-C(19)-C(22)	63.3(6)
C(27)-P(2)-C(19)-C(20)	58.1(7)
C(23)-P(2)-C(19)-C(20)	-47.4(7)
Pd(1)-P(2)-C(19)-C(20)	-177.7(5)
C(27)-P(2)-C(23)-C(26)	88.8(6)
C(19)-P(2)-C(23)-C(26)	-164.2(5)
Pd(1)-P(2)-C(23)-C(26)	-37.1(6)
C(27)-P(2)-C(23)-C(25)	-151.7(6)
C(19)-P(2)-C(23)-C(25)	-44.6(7)
Pd(1)-P(2)-C(23)-C(25)	82.5(6)
C(27)-P(2)-C(23)-C(24)	-29.1(6)
C(19)-P(2)-C(23)-C(24)	77.9(6)
Pd(1)-P(2)-C(23)-C(24)	-155.0(5)

References

- (1) Jew, S.-s.; Kim, H.-o.; Jeong, B.-s.; Park, H.-g. *Tetrahedron: Asymmetry* **1997**, 8, 1187-1192.
- (2) Shi, X. ; Attygalle, A. B.; Xu, S.-C.; Ahmad, V. U.; Meinwald, J. *Tetrahedron* **1996**, 52, 6859-6868.
- (3) Netherton, M. R.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, 41, in press.
- (4) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, 28, 342-345.
- (5) Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, 28, 113-119. See also: Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, 98, 5850-5858.