Supporting Information

Palladium Complexes Based on Ylide-Functionalized Phosphines (YPhos): Broadly Applicable High-Performance Precatalysts for the Amination of Aryl Halides at Room Temperature

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1. Experimental Details

1.1 General methods

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried using an MBraun SPS-800 (THF, toluene and pentane) or dried in accordance with standard procedures. \(^1\)H, \(^{13}\)C\(^{\text{[H]}}\), \(^{31}\)P\(^{\text{[H]}}\) NMR spectra were recorded on Avance-400 spectrometers at 25 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (J) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, br = broad signal, vbr = very broad signal. Signal assignment was supported by APT, HSQC and HMBC. Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer. IR-Spectra were recorded on a Thermo Nicolet iS5 FT-IR in transmission mode with a Specac “Omni-cell” with KBr plates and a 0.1 mm spacer or with an ATR module at 22 °C. Column chromatography was performed on a Reveleris X2 (BUCHI) Flash Chromatography- System using Reveleris packed columns. Melting Points were collected on a Stuart SMP 30 with a heat up speed of 2 °C per minute. Chlorodicyclohexylphosphine was prepared according to published procedures.\(^1\) All other reagents were purchased from Umicore, Sigma-Aldrich, ABCR, Rockwood Lithium or Acros Organics and used without further purification.

1.2 Ligand and Gold Complex Preparation

1.2.1 Preparation of L2

\[ \text{Ph} \quad \text{Cy}_3\text{P}^+ \quad \text{PCy}_2 \]

6.00 g (13.3 mmol, 1 eq.) benzyltricyclohexylphosphonium bromide were suspended in 120 ml THF. Slowly 5.63 ml (13.3 mmol, 1 eq.) n-BuLi (2.38 M in hexane) was added to the suspension. The suspension was stirred for 40 min and then 3.68 ml (4.02 g; 17.3 mmol; 1.3 eq.) Cy\(_2\)PCl were added. The suspension was stirred for 40 min at room temperature. The solid was filtered off and washed twice with 50 ml THF and dried in vacuo (7.73 g). The solid and 1.72 g (15.3 mmol) potassium tert-butanoate were suspended in 120 ml toluene. The suspension was stirred for 16 h and then heated to 100 °C for 1 h. The hot solution was filtered off and cooled to room temperature. The cooled solution was concentrated to 40 ml in vacuo until a solid precipitated. The suspension was reheated to 100 °C and stirred for 1 h. The resulting solution was first cooled to room temperature and then to -30 °C for 16 h. The cold solid was filtered off and washed 3 times with 50 ml cold pentane. The solid was dried in vacuo and the product was obtained as a white solid (5.99 g, 10.56 mmol, 80 %).

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) δ = 0.99 – 1.20 (m, 9H, CH\(_2\), PCy\(_2\), H\(_3\) + H\(_4\) PCy\(_3\), H\(_3\) + H\(_4\)), 1.22 – 1.63 (m, 19H, CH\(_2\), PCy\(_2\), H\(_2\) + H\(_3\) + H\(_4\) PCy\(_3\), H\(_2\) + H\(_3\) + H\(_4\)), 1.63 – 1.89 (m, 12H, CH\(_2\), PCy\(_2\), H\(_3\) PCy\(_3\), H\(_2\) + H\(_3\) + H\(_4\)), 1.89 – 2.08 (m, 10H, CH\(_2\), PCy\(_2\), H\(_2\) + H\(_3\) PCy\(_3\), H\(_1\) + H\(_3\)), 2.34 – 2.52 (m, 5H, CH, PCy\(_2\), H\(_2\), PCy\(_2\), H\(_1\)), 7.01 – 7.08 (m, 1H, CH, Ph, para), 7.24 – 7.32 (m, 2H, CH, Ph, meta), 7.40 – 7.47 (m, 2H, CH, Ph, ortho) ppm.

\(^{13}\)C\(^{\text{[H]}}\)-NMR (101 MHz, C\(_6\)D\(_6\)): δ = 20.5 (dd, \(^1\)JC\(_P\) = 104.6 Hz, \(^1\)JC\(_P\) = 28.1 Hz, P-C\(^-\)-P), 26.8 – 27.0 (m, CH\(_2\), PCy\(_2\), C\(_4\)), 27.5 – 27.7 (m, CH\(_2\), PCy\(_2\), C\(_4\)), 28.0 (d, \(^3\)JC\(_P\) = 11.1 Hz, CH\(_2\), PCy\(_3\), C\(_3\)), 28.2 (d, \(^3\)JC\(_P\) = 9.1 Hz, CH\(_2\), PCy\(_2\), C\(_3\)), 28.7 – 29.1 (m, CH\(_2\), PCy\(_2\), C\(_3\) PCy\(_3\), C\(_3\)), 31.9 (d, \(^2\)JC\(_P\) = 13.2 Hz, CH\(_2\), PCy\(_2\), C\(_2\)), 33.2 (d, \(^2\)JC\(_P\) = 16.3 Hz, CH\(_2\), PCy\(_2\), C\(_2\)), 35.5 (dd, \(^1\)JC\(_P\) = 49.0 Hz, \(^3\)JC\(_P\) = 8.8 Hz, CH, PCy\(_3\), C\(_1\)), 39.9 (dd, \(^1\)JC\(_P\) = 14.3 Hz, \(^3\)JC\(_P\) = 5.0 Hz, CH, PCy\(_2\), C\(_1\)), 122.5 – 122.8 (m, CH, Ph, para), 127.9 – 128.2 (m, CH, Ph, meta), 133.6 (d, \(^3\)JC\(_P\) = 6.3 Hz, CH, Ph, ortho), 146.0 (dd, \(^2\)JC\(_P\) = 10.7 Hz, \(^2\)JC\(_P\) = 2.3 Hz, C, Ph) ppm. \(^{31}\)P\(^{\text{[H]}}\)-NMR (162.1 MHz, C\(_6\)D\(_6\)): δ = -5.2 (d, \(^2\)JP = 132.1 Hz, PCy\(_3\)), 21.6 (d, \(^2\)JP = 132.1 Hz, PCy\(_3\)) ppm. CHNS: Calculated: C: 78.40, H: 10.67. Measured: C: 78.61, H: 10.60. IR (ATR): 2915 (s), 2845 (s), 1585 (m), 1478 (m), 1443 (m), 1230 (m), 1171 (w), 1006 (s), 977 (m), 885 (s), 845 (m), 703 (s), 651 (w), 540 (s), 527 (s), 506 (m), 493 (w) cm\(^{-1}\). mp: 204.5 °C.
1.2.2 Preparation of L2-AuCl

100 mg (0.18 mmol, 1.06 eq.) L2 and 53.7 mg (tetrahydrothiophene)gold (I) chloride (0.17 mmol, 1.0 eq.) were suspended in 1.5 ml pentane and stirred for 18 h. The solid was filtered off, washed twice with 5 ml pentane and dried in vacuo and obtained as a white solid (118 mg, 0.15 mmol, 89 %).

$^{1}$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ = 1.09 – 1.31 (m, 17H, CH$_2$, PCy$_2$, H$_3$ + H$_4$), 1.40 – 2.06 (m, 33H, CH$_2$PCy$_2$, H$_1$), CH$_2$:PCy$_2$, H$_2$ + H$_3$ + H$_4$ PCy$_2$, H$_2$ + H$_3$ + H$_4$), 2.16 – 2.30 (m, 2H, CH$_2$:PCy$_2$, H$_2$), 2.49 – 2.77 (m, 3H, CH$_3$PCy$_3$, H$_1$), 7.11 – 7.23 (m, 3H, CH$_2$, Ph, meta, para), 7.28 – 7.34 (m, 2H, CH, Ph, ortho) ppm. $^{13}$C($^{1}$H)-NMR (101 MHz, C$_6$D$_6$): $\delta$ = 15.2 (dd, $^{1}$JC = 104.0 Hz, $^{1}$JCP = 63.7 Hz, P-C$^\text{C}$-P), 26.8 – 26.9 (m, CH$_2$:PCy$_2$, C$_4$), 26.9 – 27.0 (m, CH$_2$:PCy$_3$, C$_4$), 27.6 (d, $^{3}$JCP = 12.9 Hz, CH$_2$:PCy$_2$, C$_3$), 28.0 (d, $^{3}$JCP = 11.6 Hz, CH$_2$:PCy$_3$, C$_3$), 28.1 (d, $^{3}$JCP = 13.0 Hz, CH$_2$:PCy$_2$, C$_3$), 29.1 (d, $^{3}$JCP = 3.0 Hz, CH$_2$:PCy$_3$, C$_3$), 31.6 – 31.7 (m, CH$_2$:PCy$_2$, C$_2$), 32.3 – 32.5 (m, CH$_2$:PCy$_2$, C$_2$), 35.3 (dd, $^{1}$JC = 49.4 Hz, $^{3}$JCP = 1.3 Hz, CH$_2$:PCy$_3$, C$_1$), 41.4 (dd, $^{1}$JC = 39.2 Hz, $^{3}$JCP = 1.2 Hz, CH$_2$:PCy$_2$, C$_1$), 125.9 – 126.1 (m, CH, Ph, para), 128.1 – 128.3 (m, CH, Ph, meta), 137.6 – 137.8 (m, CH, Ph, ortho), 140.9 (dd, $^{3}$JCP = 5.4 Hz, $^{2}$JCP = 2.4 Hz, C, Ph) ppm. $^{31}$P($^{1}$H)-NMR (162.1 MHz, CD$_2$Cl$_2$): $\delta$ = 25.0 (d, $^{3}$JP = 56.8 Hz, PCy$_3$), 30.5 (d, $^{2}$JP = 56.8 Hz, PCy$_2$) ppm.

CHNS: Calculated: C: 55.60, H: 5.57. Measured: C: 55.44, H: 7.897. IR (ATR): 2920 (m), 2848 (w), 1484 (m), 1200 (w), 1182 (w), 1075 (w), 1046 (w), 1021 (s), 996 (m), 913 (w), 888 (m), 847 (m), 709 (s), 543 (s), 515 (m), 497 (w), 480 (m) cm$^{-1}$. mp: 218.2 °C (decomposition).

1.3 Synthesis of the Palladium Complexes

1.3.1 Palladium Allyl Complexes

1.3.1.1 Pd$_{\text{al}}$1

1.5 g (2.97 mmol, 1 eq.) of ligand L1 was stirred with 0.54 mg (1.49 mmol, 0.5 eq.) of allylpalladium (II) chloride dimer in 10 ml of dry toluene and the solution was stirred overnight. The solid was filtered off and washed with 5 ml of dry toluene and 15 ml pentane. The solid was dried in vacuo and the product was obtained as yellow solid (1.83 mg, 2.75 mmol, 92 %).

$^{1}$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ = 1.12 – 1.58 (m, 25H, CH$_2$:PCy$_5$ + PCy$_3$), 1.62 (dd, $^{3}$JHP = 12.4 Hz, $^{3}$JHP = 8.3 Hz, 3H, CH$_3$), 1.67 – 2.05 (m, 25H, CH$_2$:PCy$_5$ + PCy$_3$), 2.10 – 2.24 (m, 2H, CH$_2$:PCy$_5$, H$_1$), 2.43 – 3.70 (vbr, 2H, CH$_2$:C$_6$H$_5$), 2.54 – 2.72 (m, 3H, CH$_2$:PCy$_5$, H$_1$), 3.54 (dd, $^{2}$JHH = 13.7 Hz, $^{3}$JHH = 8.5 Hz, 1H, CH$_2$:C$_6$H$_5$), 4.25 – 4.40 (m, 1H, CH$_2$:C$_6$H$_5$), 5.19 – 5.41 (m, 1H, CH$_2$:C$_6$H$_5$) ppm. $^{13}$C($^{1}$H)-NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ = -2.7 (dd, $^{1}$JCP = 112.1, $^{1}$JCP = 46.8 Hz, P-C-P), 15.5 – 15.8 (m, CH$_3$), 26.9 (d, $^{3}$JCP = 1.5 Hz, CH$_2$:PCy$_5$, C$_4$), 27.2 – 27.5 (m, CH$_2$:PCy$_5$, C$_4$), 27.8 (d, $^{3}$JCP = 13.4 Hz, CH$_2$:PCy$_5$, C$_3$), 28.1 (d, $^{3}$JCP = 11.3 Hz, CH$_2$:PCy$_3$, C$_3$), 28.60 (d, $^{3}$JCP = 9.9 Hz, CH$_2$:PCy$_3$, C$_3$), 28.63 (d, $^{3}$JCP = 2.6 Hz, CH$_2$:PCy$_3$, C$_3$), 30.0 – 30.5 (m, CH$_2$:PCy$_3$, C$_3$), 31.2 (d, $^{2}$JCP = 5.2 Hz, CH$_2$:PCy$_3$, C$_3$), 32.7 – 36.6 (m, CH$_2$:PCy$_3$, C$_3$), 38.4 – 39.6 (br, CH$_2$:PCy$_3$, C$_3$), 52.5 – 52.9 (m, CH$_2$:C$_6$H$_5$), 79.5 (d, $^{2}$JCP = 28.4 Hz, CH$_2$:C$_6$H$_5$), 114.9 (d, $^{2}$JCP = 4.4 Hz, CH$_2$:C$_6$H$_5$) ppm. $^{31}$P($^{1}$H)-NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ = 20.5 (d, $^{3}$JP = 63.5 Hz, PCy$_3$), 31.5 (d, $^{2}$JP = 63.5 Hz, PCy$_3$) ppm. CHNS: Calculated: C: 61.13, H: 9.23. Measured: C: 61.03, H: 9.34. IR (ATR): 2919 (s), 2846 (s), 1445 (m), 1153 (m), 1070 (w), 1046 (w), 1023 (w), 850 (w), 729 (w), 513 (w). mp: 129.8 °C (decomposition).
1.3.1.2 Pdₐ₂

340 mg (0.60 mmol, 1.03 eq.) of L₂ and 108 mg (0.29 mmol, 0.5 eq.) η²-allyl palladium(II) chloride dimer were suspended in 10 ml pentane and stirred for 30 min. The light-yellow suspension formed a yellow solid. The solid was filtered off and washed twice with 5 ml pentane and dried for 1 h in vacuo (385 mg, 0.51 mmol, 90%).

¹H-NMR (400 MHz, CD₂Cl₂): δ = 1.00 – 1.42 (m, 17H, CH₂, PCy₂ + PCy₃), 1.45 – 1.64 (m, 6H, CH₂, PCy₃ + PCy₂), 1.64 – 1.87 (m, 18H, CH₂, PCy₂ + PCy₃), 1.88 – 2.20 (m, 11H, CH, PCy₂, H₁, CH₂, PCy₃ + PCy₂), 2.72 – 2.86 (m, 3H, CH, PCy₃, H₁), 2.48 – 3.51 (br, 2H, CH₂, C₃H₅), 3.57 – 3.68 (m, 1H, CH, C₃H₅), 4.39 – 4.49 (m, 1H, CH₂, C₃H₅), 5.38 – 5.51 (m, 1H, CH₂, C₃H₅), 7.08 – 7.18 (m, 1H, CH, Ph, para), 7.19 – 7.27 (m, 2H, CH, Ph, meta), 7.34 – 7.46 (m, 2H, CH, Ph, ortho) ppm. ¹³C(¹H)-NMR (100.6 MHz, CD₂Cl₂): δ = 16.4 (dd, ¹JC₃H₅ = 105.9 Hz, ¹JC₃H₅ = 34.1 Hz, PCP), 27.6 (m, CH₂, PCy₂, C₄), 27.7 (m, CH₂, PCy₂, C₄), 28.2 – 28.7 (m, CH₂, PCy₃ + PCy₂), 28.8 – 29.2 (m, CH₂, PCy₂), 29.7 – 30.0 (m, CH₂, PCy₃), 31.3 (d, ¹JC₃H₅ = 4.0 Hz, CH₂, PCy₂), 37.5 (dd, ¹JC₃H₅ = 105.9 Hz, ³JC₃H₅ = 34.1 Hz, CH, PCy₃, C₁), 42.3 (dd, ¹JC₃H₅ = 13.0 Hz, ³JC₃H₅ = 6.6 Hz, CH, PCy₂, C₁), 55.9 (s, CH, C₃H₅), 79.9 (d, ³JC₃H₅ = 27.9 Hz, CH₂, C₃H₅), 115.8 (d, ²JC₃H₅ = 4.2 Hz, CH₂, C₃H₅), 125.4 (s, CH, Ph, para), 128.3 (s, CH, Ph, meta), 138.1 (s, CH, Ph, ortho), 143.9 (s, C, Ph) ppm. ³¹P(¹H)-NMR (162.1 MHz, CD₂Cl₂): δ = 15.4 – 18.6 (br, PCy₂), 23.7 (d, ²JP = 66.6 Hz, PCy₂) ppm.

CHNS: Calc.: C: 63.99, H: 8.86. Measured: C: 64.21, H: 8.87. IR (ATR): 2919 (s), 284 (s), 1583 (w), 1441 (s), 1189 (m), 1009 (s), 989 (s), 886 (m), 847 (m), 706 (s), 642 (w), 538 (s), 485 (m), 471 (w) cm⁻¹. mp: 170.4 °C (decomposition).

1.3.1.3 Pdₐ₃

300 mg (0.66 mmol, 1.05 eq.) of ligand L₃ was stirred with 113 mg (0.31 mmol, 0.5 eq.) of allylpalladium (II) chloride dimer in 7 ml of toluene overnight. A yellow precipitate was filtered off in a Schlenk frit and washed with 10 ml of toluene. The product was dried in vacuo for multiple hours and obtained as a light yellow solid (350 mg, 0.55 mmol, 89%).

¹H NMR (400 MHz, CD₂Cl₂) δ = 1.02 – 1.56 (m, 15H, CH₂, cy, H₂ + H₃ + H₄), 1.21 (d, ³JMF = 13.0 Hz, 9H, CH₃, Ph, Me), 1.47 (d, ³JMF = 13.3 Hz, 9H, CH₃, Ph, Me), 1.57 – 1.67 (m, 3H, CH₂, cy, H₄), 1.68 – 1.89 (m, 9H, CH₂, cy, H₃ + CH₃), 1.84 – 1.99 (br, 3H, CH₂, cy, H₂), 2.08 – 2.20 (br, 3H, CH₂, cy, H₂), 2.69 – 2.99 (br, 3H, CH, cy, H₁), 2.91 – 3.85 (vbr, 2H, CH₂, C₃H₅), 3.56 (dd, ²JHF = 13.5 Hz, ³JHF = 8.4 Hz, 1H, CH₂, C₃H₅), 4.27 – 4.35 (m, 1H, CH₂, C₃H₅), 5.16 – 5.62 (m, 1H, CH, C₃H₅) ppm. ¹³C(¹H)-NMR (101 MHz, CD₂Cl₂) δ = 4.0 (dd, ¹JC₃H₅ = 105.1 Hz, ¹JC₃H₅ = 41.3 Hz, P-C-P), 18.0 – 19.5 (m, CH₃), 26.9 (d, ²JC₃H₅ = 1.5 Hz, CH₂, PCy₃, C₄), 27.9 (d, ³JC₃H₅ = 12.4 Hz, CH₂, cy, C₃), 28.4 (d, ³JC₃H₅ = 11.0 Hz, CH₂, cy, C₃), 29.0 (CH₂, cy, C₂), 29.6 (CH₂, cy, C₂), 31.6 (CH₃, Ph, Me), 32.9 (CH₃, Ph, Me), 34.4 (d, ¹JC₃H₅ = 48.1 Hz, CH, cy, C₁), 42.0 – 42.3 (m, C, Ph), 56.3 (d, ²JC₃H₅ = 2.4 Hz, CH₂, C₃H₅), 79.1 – 79.7 (m, CH₂, C₃H₅), 113.7 (d, ²JC₃H₅ = 3.1 Hz, CH, C₃H₅) ppm. ³¹P(¹H)-NMR (162 MHz, CD₂Cl₂) δ = 30.8 (d, ²JP = 63.4 Hz, PCy₂), 58.0 (br, PBu₃) ppm.

CHNS: Calculated: C: 58.58, H: 9.36. Measured: C: 58.85, H: 9.31. IR (ATR): 2924 (m), 2845 (m), 1447 (w), 1353 (w), 1137 (w), 1050 (w), 898 (s), 887 (s), 850 (w), 803 (w), 608 (w), 565 (w), 536 (w), 522 (w), 509 (w) ppm. mp: 152.2 °C (decomposition).
1.3.2 Palladium Cinnamyl Complexes

1.3.2.1 Pd_{cin}1

Inside the glovebox, 36.0 mg (0.070 mmol, 2 eq.) of ligand L1 and 18.5 mg (0.035 mmol, 1 eq.) of cinnamylpalladium (II) chloride dimer was added into a J. Young NMR tube and dissolved in 0.6 ml THF-d8. After 15 minutes full product conversion was observed. Due to solubility and stability issues, the product could not be isolated.

^1H NMR (400 MHz, THF) δ = 0.96 – 2.32 (m, 55H, CH_{PCy2, H1} + CH_{PCy3 + PCy2} + CH_{Ph}), 2.67 – 2.99 (m, 3H, CH_{PCy3, H1}), 3.00 – 3.48 (vbr, 2H, CH_{C3H4}), 5.01 (dd, 3J_{HH} = 13.2 Hz, 3J_{HH} = 9.0 Hz, 1H, CH_{C3H4}), 5.85 (dt, 3J_{HH} = 13.3 Hz, 3J_{HH} = 9.3 Hz, 1H, CH_{C3H4}), 7.13 – 7.25 (m, 3H, CH_{Ph}), 7.41 – 7.48 (m, 2H, CH_{Ph}) ppm. ^31P(^1H) NMR (162 MHz, THF-d8) δ = 26.5 (d, ^2J_{PP} = 63.4 Hz, PCy_{2}), 31.5 (d, ^2J_{PP} = 63.4 Hz, PCy_{3}) ppm.

1.3.2.2 Pd_{cin}2

340 mg (0.60 mmol, 1.03 eq.) of L2 and 151 mg (0.29 mmol, 0.5 eq.) c^2-cinnamyl palladium (II) chloride complex were suspended in 10 ml pentane and stirred for 30 min. An orange solid was formed immediately at the start of stirring. The solid was filtered off and washed twice with 5 ml pentane and dried for 1 h in vacuo (468 mg, 0.57 mmol, 99 %).

^1H NMR (400 MHz, CD_{2}Cl_{2}) δ = 1.10 – 1.34 (m, 17H, CH_{PCy3 + PCy2}), 1.37 – 1.51 (m, 6H, CH_{PCy3 + PCy2}), 1.57 – 1.82 (m, 19H, CH_{PCy3 + PCy2}), 1.85 - 2.06 (m, 10H, CH_{PCy2, H1}, CH_{PCy3 + PCy2}), 2.70 - 2.87 (m, 3H, CH_{PCy3, H1}), 2.92–3.18 (vbr, 2H, CH_{PCy2, C28.1}), 4.97 - 5.07 (m, 1H, CH_{PCy3, C28.2}), 5.68 - 5.85 (m, 1H, CH_{PCy3, C28.3}), 7.03 - 7.11 (m, 1H, CH_{Ph, para}), 7.12 - 7.19 (m, 2H, CH_{Ph, meta}), 7.23 - 7.38 (m, 5H, CH_{cin, Ph}), 7.41 - 7.47 (m, 2H, CH_{Ph, ortho}) ppm. ^31C(^1H) NMR (101 MHz, CD_{2}Cl_{2}) δ = 27.1 - 27.2 (m, CH_{PCy3}), 27.2 - 27.4 (m, CH_{PCy2}), 27.9 - 28.3 (m, CH_{PCy3 + PCy2}), 28.5 – 28.8 (m, CH_{PCy3}), 29.2 – 29.7 (m, CH_{PCy3 + PCy2}), 31.0 – 31.2 (m, CH_{PCy2}), 37.5 (d, ^1J_{CP} = 48.2 Hz, C_{ cin}), 42.3 (d, ^1J_{CP} = 16.2 Hz, C_{ PCy2}), 51.0 (d, ^1J_{CP} = 1.3 Hz, CH_{ cin, C28.1}), 98.1 – 98.8 (m, CH_{ cin, C28.2}), 109.4 – 109.8 (br, CH_{ cin, C28.3}), 125.1 (s, CH_{ Ph, para}), 127.7 (s, CH_{ cin, Ph}), 127.9 (s, CH_{ cin, Ph}), 128.3 (s, CH_{ Ph, meta}), 138.0 (s, CH_{ Ph, ortho}), 138.1 – 138.4 (m, C_{ cin, C28.3}), 143.5 (s, C_{ Ph}) ppm. The signal for the anionic carbon atom cannot be found. ^31P(^1H)-NMR (162.1MHz, CD_{2}Cl_{2}): δ = 21.5 – 24.7 (vbr, PCy_{2}), 23.7 (d, ^2J_{PP} = 59.9 Hz, PCy_{3}) ppm. CHNS: Calculated: C: 66.90, H: 8.42. Measured: C: 66.74, H: 8.651. IR (ATR): 2925 s, 2846 m, 1584 w, 1480 s, 1443 m, 1201 m, 1172 m, 1127 w, 1010 s, 990 s, 884 w, 845 w, 756 s, 728 s, 708 m, 645 w, 546 s, 532 s, 515 s, 453 w cm^{-1}. mp: 185.4°C (decomposition).

1.3.2.3 Pd_{cin}3

3.0 g (6.6 mmol, 2.05 eq.) of ligand L3 and 1.67 g (3.2 mmol, 1 eq.) of cinnamylpalladium (II) chloride dimer was dissolved in 20 ml of dry THF and stirred under an immediate color change from light yellow to dark orange. The solution was stirred for approximately 5 minutes until all yellow solid was dissolved in a dark brown solution, the solvent was then removed in vacuo. The solid was filtered off and washed with 15 ml of dry pentane. The solid was dried under reduced pressure and the product was obtained as an orange solid (4.2 g, 5.83 mmol, 90 %).
**1.3.3 Palladium Indenyl Complexes**

### 1.3.3.1 PdInd1

300 mg (0.59 mmol, 1.05 eq.) of ligand L1 and 177 mg (0.28 mmol, 0.5 eq.) of n°-1-tert-butylindenyl palladium chloride dimer were added into a Schlenk flask and suspended with 10 ml of dry pentane. The solid was filtered off and washed with 10 ml of dry THF and 10 ml of dry pentane. The brown solid was dried in vacuo and 360 mg (0.44 mmol, 78%) were obtained. The product contains 2.5 weight-% of Pd metal, which could not be removed, since the product is insoluble in all common solvents.

**1H NMR** (400 MHz, THF-d8, 320 K) δ = 1.54 (s, 9H, CH3, tBu), 1.00 – 2.42 (m, 51H, CH2, PCy2 + PCy3 + CH2, PCy2), 1.58 – 1.69 (m, 3H, CH3, Me), 2.62 – 3.09 (m, 3H, CH2, PCy2, H1), 4.57 – 4.79 (m, 1H, CH2, tBu), 6.72 (dd, JHH = 3.0 Hz, 1H, CH2, tBu), 6.79 (t, JHH = 7.4 Hz, 1H, CH3, tBu), 6.83 – 6.90 (m, JHH = 7.4 Hz, 1H, CH3, tBu), 6.97 (d, JHH = 7.4 Hz, 1H, CH3, tBu), 7.45 (d, JHH = 7.7 Hz, 1H, CH3, tBu). 13C (1H) NMR was not possible due to a high insolubility of the compound in most common deuterated solvents. 31P (1H) NMR (162 MHz, THF-d8, T = 320 K) δ = 29.2 – 30.2 (br, PCy2), 31.7 (d, JPP = 55.7 Hz, PCy2, ppm IR (ATR): 2917 (s), 2845 (s), 1443 (s), 1195 (w), 1158 (m), 1110 (w), 1048 (m), 1000 (w), 918 (vs), 899 (m), 892 (m), 846 (m), 826 (m), 759 (s), 738 (w), 710 (m), 592 (w), 536 (w), 516 (m). mp: 152.2 °C (decomposition). CHNS: Calculated: C: 66.08, H: 9.00, Calculated with 2.5 weight-% of Pd metal: C: 64.41, H: 8.77. Measured: C: 64.47, H: 8.797.

### 1.3.3.2 PdInd2

340 mg (0.60 mmol, 1.03 eq.) L2 and 179 mg (0.29 mmol, 0.5 eq.) p-tert-butylidenylpalladium(II) chloride dimer were suspended in 30 ml of pentane and stirred for 16 h. After 10 min a dark bronze colored solid formed which was filtered off and washed two times with 10 ml pentane. The solvent was removed in vacuo and a dark bronze colored solid was obtained (399 mg, 0.45 mmol, 80%).

**1H NMR** (400 MHz, THF-d8) δ = 1.07 – 2.22 (m, 61H, CH2, PCy2, H1, CH2, PCy3 + PCy2, CH3, tBu), 2.54 – 3.34 (br, 3H, CH3, PCy3, H1), 4.78 – 5.04 (m, 1H, CH3, ind, HA), 6.63 – 6.69 (m, 1H, CH3, ind, Hb), 6.74 – 6.82 (m, 1H, CH3, arom), 6.84 – 6.90 (m, 1H, CH3, arom), 6.98 – 7.10 (m, 2H, CH3, arom), 7.12 – 7.22 (m, 1H, CH3, arom), 7.31 – 7.55 (vbr, 2H, CH3, arom).
7.41 – 7.47 (m, 1H, CH₃), ppm. $^{13}$C\(^{1}\)H-NMR (100.6 MHz, THF-d₈) δ = 26.0 – 29.7 (m, CH₂, PCy3 + PCy₂), 30.4 (s, CH₃, fBu), 34.5 (s, C, fBu), 36.6 (d, $^1\text{JC}P$ = 41.2 Hz, CH, PCy₃), 63.8 – 65.2 (br, CH, CA), 109.0 – 111.3 (br, CH, CB), 117.3 (s, CH, arom), 120.4 (s, CH, arom), 123.4 – 123.8 (m, CH, arom), 124.2 (s, CH, arom), 124.7 (s, CH, arom), 126.5 – 127.9 (s, CH, arom) 136.4 – 137.9 (br, CH, arom), 139.2 (s, CH, arom), 141.8 – 142.3 (br, CH, arom), 142.6 – 143.2 (br, CH, arom) ppm. The signal for the anionic carbon atom as well as the ipso carbon atom of PCy₃ cannot be found. $^{31}$P\(^{1}\)H-NMR (162.1 MHz, THF-d₈): δ = 17.7 – 31.4 (br, PCy₃), 23.5 (d, $^3\text{J}_{PP}$ = 58.3 Hz, PCy₃) ppm. CHNS: Calculated: C: 68.25, H: 8.59. Measured: C: 67.95, H: 8.374. IR (ATR): 2922 (s), 2851 (w), 1584 (w), 1444 (m), 1191 (m), 1010 (s), 990 (s), 885 (s), 848 (m), 743 (s), 707 (s), 642 (w), 538 (s), 473 (s), 418 (m) cm\(^{-1}\). mp: 170.6 °C (decomposition).

### 1.4 Catalysis: Procedure of the Test Reactions and Detailed Results

#### 1.4.1 Procedure

A 5 ml vial with a rubber cap and a stirring bar was charged in a glovebox with 189 mg (1,69 mmol, 2 eq.) of potassium tert-butoxide and 143 mg (0.85 mmol, 1 eq.) of 1,3,5-trimethoxybenzene. The vial was taken outside of the glovebox and 4 ml of tetrahydrofuran, 0.1 ml (107.6 mg, 0.85 mmol, 1 eq.) of 4-chlorotoluene and 0.92 mmol (1.1 eq.) of the amine were added via syringe. A second vial was charged with the appropriate amount of precatalyst or in case of L-Pd(dba)₃, an equimolar amount of the free ligand and tris(dibenzylideneacetone)dipalladium(0). The catalyst was dissolved in 0.5 ml of THF and stirred for 30 minutes. The catalyst solution was added to the reaction mixture and stirred at room temperature. For reaction monitoring, small aliquots of the reaction mixture were quenched with 0.2 ml of water and the organic phase was extracted. The solution was filtered through a pipette, the solvent was allowed to evaporate, and the residue was dissolved in CDCl₃ for recording an $^1$H NMR spectrum. The conversion was determined by integration of the product peaks in comparison to 1,3,5-trimethoxybenzene as the standard reagent.

#### 1.4.2 Test Reactions: Full Results

| product | cat | Time [h] | Yield [%] | product | cat | Time [h] | Yield [%] |
|---------|-----|----------|-----------|---------|-----|----------|-----------|
| 3aa     | L₁+Pd₂(dba)₃ | 1 (6) | >99 | L₁+Pd₂(dba)₃ | 1 (6) | >99 |
|         | L₂+Pd₂(dba)₃ | 6 (6) | >99 | L₂+Pd₂(dba)₃ | 6 (6) | >99 |
|         | L₃+Pd₂(dba)₃ | 24 (6) | 57 | L₃+Pd₂(dba)₃ | 24 (6) | 31 |
|         | Pₐ₁      | 1 (6) | >99 | Pₐ₁      | 1 (6) | 65 |
|         | Pₐ₂      | 1 (6) | >99 | Pₐ₂      | 1 (6) | 66 |
|         | Pₐ₃      | 6 (6) | >99 | Pₐ₃      | 6 (6) | 66 |
|         | Pₐ₄      | 1 (6) | >99 | Pₐ₄      | 1 (6) | 55 |
|         | Pₐ₅      | 1 (6) | >99 | Pₐ₅      | 1 (6) | 55 |
|         | Pₐ₆      | 1 (6) | >99 | Pₐ₆      | 1 (6) | 55 |
| 3ab     | L₁+Pd₂(dba)₃ | 1 (6) | 41 (51) | L₁+Pd₂(dba)₃ | 1 (6) | >99 |
|         | L₂+Pd₂(dba)₃ | 1 (6) | 76 (98) | L₂+Pd₂(dba)₃ | 24 (6) | 71 |
|         | L₃+Pd₂(dba)₃ | 1 (6) | 37 (44) | L₃+Pd₂(dba)₃ | 24 (6) | 63 |
|         | Pₐ₁      | 1 (6) | >99 | Pₐ₁      | 1 (6) | >99 |
|         | Pₐ₂      | 1 (6) | >99 | Pₐ₂      | 1 (6) | >99 |
|         | Pₐ₃      | 1 (6) | >99 | Pₐ₃      | 1 (6) | >99 |
|         | Pₐ₄      | 1 (6) | >99 | Pₐ₄      | 1 (6) | >99 |
|         | Pₐ₅      | 1 (6) | >99 | Pₐ₅      | 1 (6) | >99 |
|         | Pₐ₆      | 1 (6) | >99 | Pₐ₆      | 1 (6) | >99 |

Supporting Information
1.5 Isolations and gram-scale applications (aryl chlorides)

1.5.1 General procedure for the small-scale isolation

4.3 mmol (0.5 mL, 1 eq.) of 4-chlorotoluene, 4.7 mmol (1.1 eq.) of the corresponding amine as well as 8.5 mmol (954 mg, 2.0 eq.) potassium tert-butoxide were added into a Schlenk flask and dissolved in 15 ml THF. 21.3 μmol (0.5 mol%; 1.0 mol% for 3ad) of catalyst dissolved in 2.5 ml THF were added to the solution and stirred for 1 h (6 h for 3ad). The reaction was quenched by addition of 10 ml water. The phases were separated, and the aqueous phase was washed two times with 10 ml ethyl acetate. The combined organic phases were dried over sodium sulfate. The crude product was purified via column chromatography (12 g silica-packed weld column; 0-30% EtOAc in hexane).

Coupling reactions with other aryl halides were performed in a similar manner with a 1:1.1 ratio of aryl halide and amine.

\[
\begin{align*}
\text{Yield: 0.798 g (4.05 mmol; 95%)} & \text{ obtained as a pale-yellow oil.} \\
\text{^1H NMR (400 MHz, CDCl}_3) \delta = 2.44 \text{ (s, 3H, } \text{CH}_3) \text{, 3.39 (s, 3H, } \text{-NCH}_3) \text{, 6.98 (t, } \text{3}_\text{JHH} = 7.3 \text{ Hz, 1H, ArH}) \text{,} \\
& 7.05 \text{ (d, } \text{3}_\text{JHH} = 7.9 \text{ Hz, 2H, ArH}) \text{, 7.12 (d, } \text{3}_\text{JHH} = 8.4 \text{ Hz, 2H, ArH}) \text{, 7.23 (d, } \\
& \text{3}_\text{JHH} = 8.3 \text{ Hz, 2H, ArH}) \text{, 7.35 (dd, } \text{3}_\text{JHH} = 8.5 \text{ Hz, } \text{3}_\text{JHH} = 7.4 \text{ Hz, 2H, ArH}) \text{ ppm.} \\
\text{^13C(^1H)-NMR (100.6 MHz, CDCl}_3) \delta = 20.8 \text{ (s, CH}_3) \text{, 40.3 (s, } \text{-NCH}_3) \text{, 118.3 (s, ArC) \text{, 119.9 (s, ArC),} } \\
& 122.6 \text{ (s, ArC), 129.1 (s, ArC), 130.0 (s, ArC), 132.0 (s, ArC), 146.7 (s, ArC), 149.4 (s, ArC) ppm.} \\
\end{align*}
\]

Spectral data obtained for the compound are in good agreement with the reported data.²

\[
\begin{align*}
\text{Yield: 0.623 g (3.82 mmol; 89%)} & \text{ obtained as a pale-yellow oil.} \\
\text{^1H NMR (400 MHz, CDCl}_3) \delta = 1.03 \text{ (t, } \text{JHCH} = 7.3 \text{ Hz, 3H, CH}_3) \text{, 1.42 - 1.70 (m, 4H, } \text{CH}_2) \text{, 2.32 (s, 3H, } \text{CH}_3) \text{, 3.15 (t, } \\
& \text{JHCH} = 7.1 \text{ Hz, 2H, CH}_2) \text{, 3.50 (br, 1H, NH), 6.60 (d, } \text{JHCH} = 8.4 \text{ Hz, 2H,} \\
\end{align*}
\]

N-n-butyl-4-methylaniline, 3ab
Supporting Information

S9

ArH), 7.06 (d, 3JHH = 8.3 Hz, 2H, ArH) ppm. 13C(1H)-NMR (100.6 MHz, CDCl₃) δ = 14.0 (s, CH₃), 20.4 (s, CH₂), 20.4 (s, CH₃), 31.8 (s, CH₂), 44.0 (s, CH₂), 112.9 (s, ArC), 126.1 (s, ArC), 129.7 (s, ArC), 146.4 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.³

N-tert-butyl-4-methylaniline, 3ac

Yield: 0.620 g (3.80 mmol; 89%) obtained as a pale-yellow oil. ¹H NMR (400 MHz, CDCl₃) δ = 1.37 (s, 9H, CH₃, βBu), 2.33 (s, 3H, CH₂), 3.28 (br, 1H, NH), 6.78 (d, 3JHH = 8.4 Hz, 2H, ArH), 7.06 (d, 3JHH = 8.2 Hz, 2H, ArH) ppm. ¹³C(¹H)-NMR (100.6 MHz, CDCl₃) δ = 20.5 (s, CH₃), 30.1 (s, CH₂), 51.7 (s, C, βBu), 119.0 (s, ArC), 128.4 (s, ArC), 129.4 (s, ArC), 144.2 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.⁴

N-iso-propy-4-methylaniline, 3ad

Yield: 0.441 g (2.96 mmol; 69%) obtained as a pale-yellow oil. ¹H NMR (400 MHz, CDCl₃) δ = 1.26 (d, 3JHH = 6.3 Hz, 6H, CH₃, Pr), 2.32 (s, 3H, CH₂), 3.32 (br, 1H, NH), 3.56 – 3.82 (m, 1H, CH, Pr), 6.59 (d, 3JHH = 8.4 Hz, 2H, ArH), 7.06 (d, 3JHH = 8.2 Hz, 2H, ArH) ppm. ¹³C(¹H)-NMR (100.6 MHz, CDCl₃) δ = 20.4 (s, CH₃), 23.0 (s, CH₂, Pr), 44.4 (s, CH₂, Pr), 113.5 (s, ArC), 126.1 (s, ArC), 129.8 (s, ArC), 145.3 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.⁵

N,N-diethyl-4-methylaniline 3ae

Yield: 0.603 g (3.69 mmol; 86%) obtained as a pale-yellow oil. ¹H NMR (400 MHz, CDCl₃) δ = 1.31 (t, 3JHH = 7.1 Hz, 6H, CH₂, Et), 2.43 (s, 3H, CH₂), 3.60 – 3.77 (q, 3JHH = 7.1 Hz, 4H, CH₂, Et), 6.80 (d, 3JHH = 8.6 Hz, 2H, ArH), 7.20 (d, 3JHH = 8.5 Hz, 2H, ArH) ppm. ¹³C(¹H)-NMR (100.6 MHz, CDCl₃) δ = 12.6 (s, CH₂, Et), 20.2 (s, CH₂), 44.5 (s, CH₂, Et), 112.6 (s, ArC), 124.8 (s, ArC), 129.8 (s, ArC), 145.9 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.⁶

1-(p-tolyl)piperidine,3af

Yield: 0.718 g (4.09 mmol; 96%) obtained as a pale-yellow oil. ¹H NMR (400 MHz, CDCl₃) δ = 1.58 – 1.70 (m, 2H, CH₂, Pip), 1.73 – 1.87 (m, 4H, CH₂, Pip), 2.36 (s, 3H, CH₂), 2.98 – 3.34 (m, 4H, CH₂, Pip), 6.95 (d, 3JHH = 8.3 Hz, 2H, ArH), 7.15 (d, 3JHH = 8.0 Hz, 2H, ArH) ppm. ¹³C(¹H)-NMR (100.6 MHz, CDCl₃) δ = 20.5 (s, CH₂), 24.4 (s, CH₂), 26.0 (s, CH₂), 51.4 (s, CH₂), 117.0 (s, ArC), 128.7 (s, ArC), 129.6 (s, ArC), 150.3 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.⁷
N-benzyl-4-methylaniline, 3ag

**Yield:** 0.813 g (4.12 mmol; 96%) obtained as a pale-yellow oil. 1H NMR (400 MHz, d8-DCM) δ = 2.63 (s, 3H, CH3), 4.34 (br, 1H, NH), 4.66 (s, 2H, CH2), 6.93 (d, 3JHH = 8.5 Hz, 2H, ArH), 7.37 (d, 3JHH = 8.4 Hz, 2H, ArH), 7.60 – 7.80 (m, 5H, ArH) ppm. 13C{1H}-NMR (100.6 MHz, d8-DCM) δ = 20.8 (s, CH3), 48.9 (s, CH2), 113.5 (s, ArC), 127.1 (s, ArC), 127.6 (s, ArC), 128.0 (s, ArC), 129.1 (s, ArC), 130.3 (s, ArC), 140.6 (s, ArC), 146.6 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported.8

### 1.5.2 General procedure for gram-scale applications

8.0 mmol (1 eq.) of the aryl halide, 8.8 mmol (1.1 eq.) of the corresponding amine as well as 16 mmol (1.80 g, 2.0 eq.) potassium tert-butoxide were added into a Schlenk flask and dissolved in 30 ml THF. 40.0 µmol (35.2 mg; 0.5 mol%) of catalyst Pind2 dissolved in 4.0 ml THF were added to the solution and stirred for 6 h. The reaction was quenched by addition of 20 ml water. The phases were separated, and the aqueous phase was washed two times with 20 ml ethyl acetate. The combined organic phases were dried over sodium sulfate. After filtration and evaporation of the solvent, the crude product was purified via column (12 g silica-packed weld column; 0-30% EtOAc in hexane).

#### 4-(4-(methoxy-butyl)phenyl)piperidine, 3ef

**Yield:** 1.51 g (7.89 mmol; 99%) obtained as a pale-yellow oil. 1H NMR (400 MHz, CDCl3) δ = 1.52 – 1.65 (m, 2H, CH2, Pip), 1.70 – 1.84 (m, 4H, CH2, Pip), 3.02 – 3.10 (m, 4H, CH2, Pip), 3.78 (s, 3H, -OCH3), 6.86 (d, 3JHH = 9.2 Hz, 2H, ArH), 6.95 (d, 3JHH = 9.1 Hz, 2H, ArH) ppm. 13C{1H}-NMR (100.6 MHz, CDCl3) δ = 24.2 (s, CH2), 26.1 (s, CH2), 52.2 (s, CH2), 55.4 (s, -OCH3), 114.3 (s, ArC), 118.7 (s, ArC), 146.9 (s, ArC), 153.5 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported.7

#### 4-(4-(methoxy-butyl)phenyl)morpholine, 3eh

**Yield:** 1.50 g (7.77 mmol; 98%) obtained as a white solid. 1H NMR (400 MHz, CDCl3) δ = 3.00 – 3.12 (m, 4H, CH2, Morph), 3.77 (s, 3H, -OCH3), 3.82 – 3.91 (m, 4H, CH2, Morph), 6.83 – 6.92 (m, 4H, ArH) ppm. 13C{1H}-NMR (100.6 MHz, CDCl3) δ = 50.9 (s, CH2), 55.6 (s, -OCH3), 67.1 (s, CH2), 114.6 (s, ArC), 117.9 (s, ArC), 145.7 (s, ArC), 154.1 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported.7

#### 4-(4-(tert-butyl)phenyl)piperidine, 3ff

**Yield:** 1.64 g (7.52 mmol; 94%) obtained as a pale-yellow solid. 1H NMR (400 MHz, CDCl3) δ = 1.43 (s, 9H, CH3, tBu), 1.63 – 1.74 (m, 2H, CH2, Pip), 1.76 – 1.89 (m, 4H, CH2, Pip), 3.17 – 3.30 (m, 4H, CH2, Pip), 7.01 (d, 3JHH = 8.9 Hz, 2H, ArH), 7.39 (d, 3JHH = 8.9 Hz, 2H, ArH) ppm. 13C{1H}-NMR (100.6 MHz, CDCl3) δ = 24.4 (s, CH2), 26.1 (s, CH2), 31.6 (s, CH3, tBu), 34.0 (s, C, tBu), 51.0 (s, CH2), 116.3 (s, ArC), 125.8 (s, ArC), 141.9 (s, ArC), 150.1 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.9
4-(4-(tert-butyl)phenyl)morpholine, 3fh

Yield: 1.72 g (7.86 mmol; 99%) obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ = 1.31 (s, 9H, CH$_3$, pBu), 3.10 – 3.18 (m, 4H, CH$_2, \text{Morph}$), 3.82 – 3.90 (m, 4H, CH$_2, \text{Morph}$), 6.88 (d, $^3$J$_{HH}$ = 8.9 Hz, 2H, ArH), 7.32 (d, $^3$J$_{HH}$ = 8.9 Hz, 2H, ArH) ppm. $^{13}$C($^1$H)-NMR (100.6 MHz, CDCl$_3$) δ = 31.6 (s, CH$_3$, pBu), 34.1 (s, C, pBu), 49.7 (s, CH$_2$), 67.2 (s, CH$_2$), 115.6 (s, ArC), 126.1 (s, ArC), 142.9 (s, ArC), 149.1 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.\(^{10}\)

4-(pyridin-2-yl)piperidine, 3gf

Yield: 1.27 g (7.85 mmol; 99%) obtained as a pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ = 1.57 (s, 6H, CH$_2, \text{Pip}$), 3.46 (s, 4H, CH$_2, \text{Pip}$), 6.43 – 6.51 (m, 1H, ArH), 6.56 (d, $^3$J$_{HH}$ = 8.6 Hz, 1H, ArH), 7.35 (ddd, J = 8.9, 7.1, 2.0 Hz, 1H, ArH), 8.10 – 8.14 (m, 1H, ArH) ppm. $^{13}$C($^1$H)-NMR (100.6 MHz, CDCl$_3$) δ = 24.7 (s, CH$_2$), 25.5 (s, CH$_2$), 46.2 (s, CH$_2$), 107.0 (s, ArC), 112.3 (s, ArC), 137.2 (s, ArC), 147.9 (s, ArC), 159.7 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.\(^{11}\)

4-(pyridin-2-yl)morpholine, 3gh

Yield: 1.29 g (7.84 mmol; 98%) obtained as a pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ = 3.39 (t, $^3$J$_{HH}$ = 5.1 Hz, 4H, CH$_2, \text{Morph}$), 3.71 (t, $^3$J$_{HH}$ = 4.9 Hz, 4H, CH$_2, \text{Morph}$), 6.42 – 6.66 (m, 2H, ArH), 7.39 (ddd, J = 9.0, 7.2, 2.0 Hz, 1H, ArH), 7.99 – 8.21 (m, 1H, ArH) ppm. $^{13}$C($^1$H)-NMR (100.6 MHz, CDCl$_3$) δ = 45.4 (s, CH$_2$), 66.6 (s, CH$_2$), 106.7 (s, ArC), 113.6 (s, ArC), 137.3 (s, ArC), 147.8 (s, ArC), 159.4 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.\(^{11}\)

1-(3,5-dimethoxyphenyl)piperidine, 3hf

Yield: 1.73 g (7.83 mmol; 98%) obtained as a pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ = 1.54 – 1.63 (m, 2H, CH$_2, \text{Pip}$), 1.66 – 1.76 (m, 4H, CH$_2, \text{Pip}$), 3.12 – 3.21 (m, 4H, CH$_2, \text{Pip}$), 3.78 (s, 6H, -OCH$_3$), 6.01 (t, J = 2.1 Hz, 1H, ArH), 6.13 (d, J = 2.2 Hz, 2H, ArH) ppm. $^{13}$C($^1$H)-NMR (100.6 MHz, CDCl$_3$) δ = 24.3 (s, CH$_2$), 25.7 (s, CH$_2$), 50.5 (s, CH$_2$), 55.0 (s, -OCH$_3$), 91.1 (s, ArC), 95.2 (s, ArC), 154.0 (s, ArC), 161.3 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.\(^{12}\)

4-(3,5-dimethoxyphenyl)morpholine, 3hh

Yield: 1.75 g (7.84 mmol; 98%) obtained as a pale-yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ = 3.10 – 3.19 (m, 4H, CH$_2, \text{Morph}$), 3.77 (s, 6H, -OCH$_3$), 3.81 – 3.89 (m, 4H, CH$_2, \text{Morph}$), 6.04 (t, J = 2.1 Hz, 1H, ArH), 6.08 (d, J = 2.1 Hz, 2H, ArH) ppm. $^{13}$C($^1$H)-NMR (100.6 MHz, CDCl$_3$) δ = 49.4 (s, CH$_2$), 55.3 (s, -OCH$_3$), 67.0 (s, CH$_2$), 91.9 (s, ArC), 94.8 (s, ArC), 153.4 (s, ArC), 161.6 (s, ArC) ppm. Spectral data obtained for the compound are in good agreement with the reported data.\(^{13}\)
1.6 General procedure for the coupling of aryl iodides and bromides (Scheme 4)

1.6.1 General Procedure for Catalysis

A 5 ml vial with a rubber cap and a stirring bar was charged in a glovebox with 189 mg (1.69 mmol, 2 eq.) of potassium tert-butoxide and 143 mg (0.85 mmol, 1 eq.) of 1,3,5-trimethoxybenzene (internal standard). The vial was taken outside of the glovebox and 3 ml of tetrahydrofurane, 0.85 mmol (1 eq.) of an aryl halide and 0.94 mmol (1.1 eq.) of the amine were added via syringe. A second vial was charged with 3.7 mg (0.5 mol%) of P$_{3}$Ph$_{2}$. The catalyst was dissolved in 0.5 ml of THF and stirred for 30 minutes. The catalyst solution was added to the reaction mixture and stirred at room temperature. For reaction monitoring, small aliquotes of the reaction mixture were quenched with 0.2 ml of water and the organic phase was extracted. The solution was filtered through a pipette, the solvent was allowed to evaporate, and the residue was dissolved in CDCl$_{3}$ for recording an $^1$H NMR spectrum. The conversion was determined by integration of the product peaks in comparison to 1,3,5-trimethoxybenzene as internal standard.

Results

| Aryl Halide | Amine | Product | Time [h] | Conversion [%] |
|-------------|-------|---------|----------|---------------|
| ![Aryl Halide](image1.png) | ![Amine](image2.png) | ![Product](image3.png) | 1 | >99 |
| ![Aryl Halide](image4.png) | ![Amine](image2.png) | ![Product](image5.png) | 1 | >99 |
| ![Aryl Halide](image6.png) | ![Amine](image7.png) | ![Product](image8.png) | 1 | >99 |
| ![Aryl Halide](image9.png) | ![Amine](image10.png) | ![Product](image11.png) | 1 | >99 |
| ![Aryl Halide](image12.png) | ![Amine](image13.png) | ![Product](image14.png) | 1 | 96 |
| ![Aryl Halide](image15.png) | ![Amine](image16.png) | ![Product](image17.png) | 3 | 99 |
1.6.2  General Procedure for Isolations

4.3 mmol (0.5 mL, 1 eq.) of an iodohalide, 4.7 mmol (1.1 eq.) of the corresponding amine as well as 8.5 mmol (954 mg, 2.0 eq.) potassium tert-butoxide were added into a Schlenk flask and dissolved in 12 ml THF. 21.3 µmol (0.5 mol%) of catalyst dissolved in 3 ml THF were added to the solution and stirred for 2 h. The reaction was quenched by addition of 10 ml water. The phases were separated, and the aqueous phase was washed three times with 10 ml ethyl acetate. The combined organic phases were dried over sodium sulfate. The crude product was purified via column chromatography (12 g silica-packed weld column; 0-30% EtOAc in hexane).

**N-benzynaphthalen-1-amine, 3bg**

Yield: 0.935 g (4.01 mmol; 94%) obtained as an off-white solid. ¹H NMR (400 MHz, CDCl₃) δ = 7.83 – 7.69 (m, 2H, ArH), 7.44 – 7.15 (m, 9H, ArH), 6.57 (d, J = 7.4 Hz, 1H, ArH), 4.65 (br s, 1H, NH), 4.43 (s, 2H, CH₂) ppm. ¹³C(¹H) NMR (101 MHz, CDCl₃) δ = 143.3, 139.2, 134.4, 128.9, 128.8, 127.9, 127.6, 126.7, 125.9, 124.9, 123.6, 120.0, 117.9, 105.0, 48.8 ppm. Spectral data obtained for the compound are in good agreement with the reported data. However, in contrast to the literature report 3cg is a solid; m.p. 70.8 °C.
**N-Isopropyl-2-methylaniline, 3cd**

Yield: 0.467 g (3.13 mmol; 74%) obtained as a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.12\) (t, \(J = 7.7\) Hz, 1H, ArH), 7.05 (d, \(J = 7.3\) Hz, 1H, ArH), 6.70 – 6.58 (m, 2H, ArH), 3.68 (hept, \(J = 6.3\) Hz, 1H, C\(\text{H}\)), 3.31 (br s, 1H, NH), 2.12 (s, 3H, ArCH\(_3\)), 1.25 (d, \(J = 6.3\) Hz, 6H, NHCH\(_3\)) ppm. \(^{13}\)C{\(^1\)H} NMR (101 MHz, CDCl\(_3\)) \(\delta = 145.5, 130.3, 127.2, 121.8, 116.5, 110.4, 44.1, 23.3, 17.7\) ppm. Spectral data obtained for the compound are in good agreement with the reported data.\(^{15}\)

**N-benzyl-2-methylbenzeneamine, 3cg**

Yield: 0.903 g (4.58 mmol; 97%) obtained as a light off-white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.45 – 7.33\) (m, 4H, ArH), 7.32 – 7.27 (m, 1H, ArH), 7.16 – 7.06 (m, 2H, ArH), 6.69 (td, \(J = 7.4\) Hz, 1.2 Hz, 1H, ArH), 6.63 (d, \(J = 8.0\) Hz, 1H, ArH), 4.39 (s, 2H, CH\(_2\)), 3.90 (br s, 1H, NH), 2.18 (s, 3H, CH\(_3\)) ppm. \(^{13}\)C{\(^1\)H} NMR (101 MHz, CDCl\(_3\)) \(\delta = 146.2, 139.6, 130.2, 128.8, 127.7, 127.4, 122.1, 117.3, 110.1, 48.4, 17.7\) ppm. Spectral data obtained for the compound are in good agreement with the reported data.\(^{16}\) However, in contrast to the literature report 3cg is a solid; m.p. 61.2 °C.

### 1.7 Kinetic studies

**Procedure:**

A 100 ml Schlenk round-bottom flask with a stirring bar was charged in a glovebox with 2 equivalents of potassium tert-butoxide and 1 equivalent of 1,3,5-trimethoxybenzene. The flask was taken outside of the glovebox and 4-chlorotoluene and piperidine were added and filled up to a volume of 24.5 mL (E1) or 25.0 mL (E2) with THF via syringe. A second vial was charged with the appropriate amount of precatalyst. The catalyst was dissolved in 0.5 ml (E1) or 5.0 ml (E2) of THF, stirred for 30 minutes. The catalyst solution was added to the reaction mixture and stirred at room temperature. For reaction monitoring, small aliquotes of the reaction mixture were taken every minute and worked up according to 1.4.1.

| Experiment 1 (E1) | Experiment 2 (E2) |
|------------------|-------------------|
| 1.00 mmol / 118 µL 4-chlorotoluene | 10.0 mmol / 1.18 mL 4-chlorotoluene |
| 1.00 mmol / 100 µL piperidine | 10.0 mmol / 1.00 mL piperidine |
| 0.5 mol% cat in THF | 0.5 mol% cat in THF |
| Total volume: 25 mL | Total volume: 30 mL |

| Experiment 3 (E3) | Experiment 4 (E4) |
|------------------|-------------------|
| 2.00 mmol / 236 µL 4-chlorotoluene | 1.00 mmol / 118 µL 4-chlorotoluene |
| 1.00 mmol / 100 µL piperidine | 2.00 mmol / 200 µL piperidine |
| 0.5 mol% cat in THF | 0.5 mol% cat in THF |
| Total volume: 25 mL | Total volume: 25 mL |
Results

Table S1. Results of the kinetic studies for the amination of \( p \)-chlorotoluene with piperidine with 0.5 mol\% \( \text{P} \text{ind}_2 \) at different concentrations.

| Time [min] | \([\text{ArCl}]:[\text{amine}] = 1:1; 0.04 \text{ M (E1)}\) | \([\text{ArCl}]:[\text{amine}] = 1:1; 0.33 \text{ M (E2)}\) | \([\text{ArCl}]:[\text{amine}] = 2:1; 0.04 \text{ M (E3)}\) | \([\text{ArCl}]:[\text{amine}] = 1:2; 0.04 \text{ M (E4)}\) |
|------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 0          | 0                                               | 0                                               | 0                                               | 0                                               |
| 0.17       | 0                                               | 10                                              | 0                                               | 0                                               |
| 1          | 8                                               | 100                                             | 14                                              | 8                                               |
| 2          | 18                                              | 100                                             | 36                                              | 17                                              |
| 3          | 29                                              | 100                                             | 58                                              | 27                                              |
| 4          | 40                                              | 100                                             | 80                                              | 38                                              |
| 5          | 54                                              | 100                                             | 94                                              | 47                                              |
| 6          | 66                                              | 100                                             | 100                                             | 55                                              |
| 7          | 75                                              | 100                                             | 100                                             | 63                                              |
| 8          | 85                                              | 100                                             | 100                                             | 71                                              |
| 9          | 93                                              | 100                                             | 100                                             | 81                                              |
| 10         | 99                                              | 100                                             | 100                                             | 86                                              |
| 11         | 100                                             | 100                                             | 100                                             | 93                                              |
| 12         | 100                                             | 100                                             | 100                                             | 99                                              |
| 13         | 100                                             | 100                                             | 100                                             | 100                                             |
| 14         | 100                                             | 100                                             | 100                                             | 100                                             |
| 15         | 100                                             | 100                                             | 100                                             | 100                                             |
| 16         | 100                                             | 100                                             | 100                                             | 100                                             |

Figure S1. Conversion-time plots for the amination of \( p \)-chlorotoluene with piperidine with \( \text{P} \text{ind}_2 \) as catalyst at different concentrations and amine:ArCl ratios. Conditions: 0.5 mol\% \( \text{P} \text{ind}_2 \), room temperature, THF. Conversion was determined by NMR spectroscopy with 1,3,5-methoxybenzene as standard.
**Supporting Information**

**Figure S2.** Determination of the initial reaction rate for the amination of p-chlorotoluene with piperidine with P$_{ind}$ as catalyst. Conditions: 0.5 mol% P$_{ind}$, RT, equiv. ArCl:amine:base = 1:1:2, THF, 0.04 mol/L. Conversion was determined by NMR spectroscopy with 1,3,5-methoxybenzene as standard.

**Figure S3.** Variable time normalization analysis with (top) excess ArCl and (bottom) excess analysis. Analysis gives an overlay of the two reaction profiles with a reaction order of 0.75 and -0.2, respectively.
2. **NMR spectra**

2.1 **NMR spectra of the ligand and palladium complexes**

2.1.1 **NMR spectra of L2**

**Figure S4.** $^{31}$P($^1$H) NMR spectrum of L2.

**Figure S5.** $^1$H NMR spectrum of L2.
Figure S6. $^{13}$C($^1$H) NMR spectrum of L2.

2.1.2 NMR spectra of L2·AuCl

Figure S7. $^{31}$P($^1$H) NMR spectrum of L2·AuCl.
Figure S8. $^1$H NMR spectrum of L2·AuCl.

Figure S9. $^{13}$C($^1$H) NMR spectrum of L2·AuCl.
2.1.3 NMR spectra of \( \text{P_{al1}} \)

**Figure S10.** \( ^{31}\text{P}(^1\text{H}) \) NMR spectrum of \( \text{P_{al1}} \). The Signals at 22 and 35 ppm correspond to the free ligand.
Figure S11. $^1$H NMR spectrum of $P_{\text{al}1}$.

Parameter | Value
---|---
1 Title | IR-ESMR-69_1200_2200_12.5M
2 Solvent | CDCl3
3 Temperature | 298.0
4 Experiment | 10
5 Number of Scans | 8/32
6 Acquisition Date | 2019-05-05T01:46:44
7 Spectrometer Frequency | 400.13
8 Nucleus | $^1$H

Figure S12. $^{13}$C ($^1$H) NMR spectrum of $P_{\text{al}1}$.

2.1.4 NMR spectra of $P_{\text{al}2}$

Parameter | Value
---|---
1 Title | SI-100_6,12201.10-Rg
2 Solvent | CDCl3
3 Temperature | 298.0
4 Experiment | 10
5 Number of Scans | 128
6 Acquisition Date | 2019-05-22T18:04:13
7 Spectrometer Frequency | 100.61
8 Nucleus | $^{13}$C
Figure S13. $^{31}$P{$^1$H} NMR spectrum of \( \text{Pa}_2 \).

Figure S14. \(^1\)H NMR spectrum of \( \text{Pa}_2 \).
Figure S15. $^{13}$C($^1$H) NMR spectrum of P$_{al2}$.

2.1.5 NMR spectra of P$_{al3}$

Figure S16. $^{31}$P($^1$H) NMR spectrum of P$_{al3}$.
Figure S17. $^1$H NMR spectrum of Pal$_3$.

Figure S18. $^{13}$C ($^1$H) NMR spectrum of Pal$_3$.

2.1.6 NMR spectra of Pal$_1$
**Figure S19.** $^{31}P(\text{H})$ NMR spectrum of reaction mixture of the formation of $P_{\text{cin}1}$. Signals at 1.0 and 30.6 ppm belong to unconsumed ligand $L1$.

**Figure S20.** $^1H$ NMR spectrum of reaction mixture of the formation of $P_{\text{cin}1}$. Signals at 1.0 and 30.6 ppm belong to unconsumed ligand $L1$. 

| Parameter | Value |
|-----------|-------|
| Title     | IR-DHPF-C1_15min_THF-d8.11 AM |
| Solvent   | THF |
| Temperature | 298.0 |
| Experiment | 1D |
| Number of Scans | 16 |
| Acquisition Date | 2018-05-03T17:15:18 |
| Spectrometer Frequency | 400.33 |
| Nucleus | $^1H$ |
2.1.7 NMR spectra of $P_{cin2}$

**Figure S21.** $^{31}P\{^1H\}$ NMR spectrum of $P_{cin2}$.

**Figure S22.** $^{31}P\{^1H\}$ NMR spectrum of $P_{cin2}$. 
Supporting Information

Figure S23. $^{13}$C($^1$H) NMR spectrum of Pcin2.

2.1.8 NMR spectra of Pcin3

Figure S24. $^{31}$P($^1$H) NMR spectrum of Pcin3 at 320 K.
Figure S25. $^1$H NMR spectrum of $P_{\text{cm}3}$ at 320 K.

Figure S26. $^{13}$C ($^1$H) NMR spectrum (APT) of $P_{\text{cm}3}$ at 320 K.
2.1.9 NMR spectra of \( \text{Pind}1 \)

Figure S27. \( ^{31}\text{P}\{\text{H}\} \) NMR spectrum of \( \text{Pind}1 \).

Figure S28. \( ^{1}\text{H} \) NMR spectrum of \( \text{Pind}1 \).
2.1.10 NMR spectra of P_{ind2}

**Figure S29.** $^{31}$P{$^{1}$H} NMR spectrum of P_{ind2}.

**Figure S30.** $^{1}$H NMR spectrum of P_{ind2}.
Figure S31. $^{13}$C($^1$H) NMR spectrum of P_{ind2}. 
2.2 NMR spectra of the isolated products

3aa, N,4-dimethyl-N-phenylaniline

Figure S32. $^1$H NMR spectrum of 3aa.

Figure S33. $^{13}$C($^1$H) NMR spectrum of 3aa.
3ab, N-butyl-4-methylaniline

**Figure S34.** $^1$H NMR spectrum of 3ab.

**Figure S35.** $^{13}$C($^1$H) NMR spectrum of 3ab.
3ac, N-tert-butyl-4-methylaniline

Figure S36. $^1$H NMR spectrum of 3ac.

Figure S37. $^{13}$C($^1$H) NMR spectrum of 3ac.
3ad, *N*-iso-propyl-4-methylaniline

Figure S38. $^1$H NMR spectrum of 3ad.

Figure S39. $^{13}$C($^1$H) NMR spectrum of 3ad.
3ae, *N,N*-diethyl-4-methylaniline

Figure S40. $^1$H NMR spectrum of 3ae.

Figure S41. $^{13}$C($^1$H) NMR spectrum of 3ae.
3af, 1-(p-tolyl)piperidine

Figure S42. $^{13}$C($^1$H) NMR spectrum of 3af.

Figure S43. $^{13}$C($^1$H) NMR spectrum of 3af.
3ag, N-benzyl-4-methylaniline

Figure S44. $^1$H NMR spectrum of 3ag.

Figure S45. $^{13}$C($^1$H) NMR spectrum of 3ag.
**N-benzynaphthalen-1-amine, 3bg**

![NMR spectra](image)

**Figure S46.** $^1$H NMR spectrum of 3bg.

**Figure S47.** $^{13}$C($^1$H) NMR spectrum of 3bg.
**N-Isopropyl-2-methylaniline, 3cd**

Figure S48. $^1$H NMR spectrum of 3cd.

Figure S49. $^{13}$C($^1$H) NMR spectrum of 3cd.
**N-benzyl-2-methylbenzeneamine, 3cg**

Figure S50. $^1$H NMR spectrum of 3cg.

Figure S51. $^{13}$C($^1$H) NMR spectrum of 3cg.
3ef, 1-(4-methoxyphenyl)piperidine

**Figure S52.** $^1$H NMR spectrum of 3ef.

**Figure S53.** $^{13}$C($^1$H) NMR spectrum of 3ef.
3eh, 4-(4-methoxyphenyl)morpholine

Figure S54. ¹H NMR spectrum of 3eh.

Figure S55. ¹³C(¹H) NMR spectrum of 3eh.
3ff, 1-(4-tert-butylphenyl)piperidine

Figure S56. $^1$H NMR spectrum of 3ff.

Figure S57. $^{13}$C($^1$H) NMR spectrum of 3ff.
3fh, 4-(4-(tert-butyl)phenyl)morpholine

Figure S58. $^1$H NMR spectrum of 3fh.

Figure S59. $^{13}$C($^1$H) NMR spectrum of 3fh.
3gf, 2-(piperidin-1-yl)pyridine

Figure S60. $^1$H NMR spectrum of 3gf.

Figure S61. $^{13}$C($^1$H) NMR spectrum of 3gf.
3gh, 4-(pyridin-2-yl)morpholine

**Figure S62.** $^1$H NMR spectrum of 3gh.

**Figure S63.** $^{13}$C($^1$H) NMR spectrum of 3gh.
3hf, 1-(3,5-dimethoxyphenyl)piperidine

| Parameter | Value |
|-----------|-------|
| 1. Title  | J7-072A_4202018.11.5d |
| 2. Solvent | CDCl3 |
| 3. Temperature | 298.1 |
| 4. Experiment | 1D |
| 5. Number of Scans | 16 |
| 6. Acquisition Date | 2019-09-03T07:37:19 |
| 7. Spectrometer Frequency | 100.57 |
| 8. Nucleus | 13C |

Figure S64. $^1$H NMR spectrum of 3hf.

Figure S65. $^{13}$C($^1$H) NMR spectrum of 3hf.
3hh, 4-(3,5-dimethoxyphenyl)morpholine

Figure S66. $^1$H NMR spectrum of 3hh.

Figure S67. $^{13}$C($^1$H) NMR spectrum of 3hh.
3. Crystal Structure Determination

3.1 General information

Data collection of all compounds was conducted with an Oxford SuperNova diffractometer. The structures were solved using direct methods, refined with the Shelx software package and expanded using Fourier techniques. The crystals of all compounds were mounted in an inert oil (perfluoropolyalkylether). Crystal structure determinations were affected at 100 K. Crystallographic data (including structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1952269-1952275 and 1978563. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].

Details on the structure solutions

\( \text{P}_{\text{al3}} \) contained a disordered allyl group with an occupancy of 0.95:0.05. It was modelled by using RIGU and SADI restraints.

\((\mu\text{-allyl})(\mu\text{-Cl})\text{Pd}(L2)_2\) contained three disordered allyl groups with occupancies of 0.62:0.38, 0.50:0.50 and 0.44:0.56. The structure contained a highly disordered free pentane molecule that was treated by using the PLATON/SQUEZZE routine. Additionally, it was a merohedral twin with an occupancy of 0.61:0.39.

Table S2. Data collection and structure refinement details for the compounds \( \text{L2}, \text{L2-AuCl} \) and \( \text{P}_{\text{al1}} \).

| Compound       | \( \text{L2} \) | \( \text{L2-AuCl} \) | \( \text{P}_{\text{al1}} \) |
|----------------|----------------|----------------|----------------|
| CCDC No.       | 1952269        | 1952270        | 1952271        |
| Formula        | \( \text{C}_{37}\text{H}_{60}\text{P}_2 \) | \( \text{C}_{39}\text{H}_{64}\text{AuCl}_5\text{P}_2 \) | \( \text{C}_{35}\text{H}_{63}\text{ClP}_2\text{Pd} \) |
| Formula weight | 566.79         | 969.05         | 687.64         |
| Temperature    | 100.05(10)     | 99.90(14)      | 100.00(14)     |
| Wave length    | 1.54184        | 1.54184        | 1.54184        |
| Crystal system | Monoclinic     | Monoclinic     | Monoclinic     |
| Space group    | \( \text{P}_2_1/n \) | \( \text{P}_2_1 \) | \( \text{P}_2_1/n \) |
| \( a \) [Å]    | 13.1189(4)     | 10.43643(13)   | 10.6583(2)     |
| \( b \) [Å]    | 17.2309(9)     | 16.0519(2)     | 15.2493(3)     |
| \( c \) [Å]    | 14.9442(6)     | 12.59762(19)   | 21.5766(4)     |
| \( \alpha \) [°] | 90             | 90             | 90             |
| \( \beta \) [°] | 98.531(3)      | 98.4531(13)    | 100.5571(19)   |
| \( \gamma \) [°] | 90             | 90             | 90             |
| Volume [Å³]    | 3340.8(2)      | 2087.48(5)     | 3447.53(11)    |
| \( Z \)        | 4              | 2              | 4              |
| Calc. density  | 1.127          | 1.542          | 1.325          |
| \( \mu \) [mm⁻¹] | 1.332          | 10.482         | 6.078          |
| \( F(000) \)   | 1248           | 984            | 1464           |
Table S3. Data collection and structure refinement details for the compounds P\textsubscript{al3} and P\textsubscript{cin2}.

| Compound | P\textsubscript{al3} | P\textsubscript{cin2} |
|----------|----------------|----------------|
| CCDC No. | 1952272 | 1952273 |
| Formula  | C\textsubscript{31}H\textsubscript{59}ClP\textsubscript{2}Pd | C\textsubscript{368}H\textsubscript{552}Cl\textsubscript{8}P\textsubscript{16}Pd\textsubscript{8} |
| Formula weight [g·mol\textsuperscript{-1}] | 635.57 | 6606.38 |
| Temperature [K] | 100.00(14) | 100(2) |
| Wave length [Å] | 1.54184 | 1.54184 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | P2\textsubscript{1}/n | Pbca |
| a [Å] | 9.87310(13) | 10.4368(4) |
| b [Å] | 13.48921(19) | 19.9071(7) |
| c [Å] | 23.5503(3) | 39.2909(16) |
| α [°] | 90 | 90 |
| β [°] | 91.5609(13) | 90 |
| γ [°] | 90 | 90 |
| Volume [Å\textsuperscript{3}] | 3135.27(7) | 8163.3(5) |
| Z | 4 | 1 |
| Calc. density [Mg·m\textsuperscript{-3}] | 1.346 | 1.344 |
| μ [mm\textsuperscript{-1}] | 6.637 | 5.231 |
| F(000) | 1352 | 3504 |
| Crystal dimensions [mm] | 0.147 x 0.039 x 0.026 | 0.048 x 0.047 x 0.040 |
| Theta range [°] | 3.755 to 72.119 | 2.249 to 74.998 |
| Index ranges | –12 ≤ h ≤ 11 | –12 ≤ h ≤ 12 |
| | –16 ≤ k ≤ 16 | –20 ≤ k ≤ 24 |
Reflections collected  35778  33504
Independent reflections  6176 \([R_{int} = 0.0420]\)  8188 \([R_{int} = 0.0696]\)
Data/Restraints/Parameter  6176 / 53 / 536  8188 / 0 / 451
Goodness-of-fit on \(F^2\)  1.012  1.058
Final \(R\) indices \([I>2\sigma(I)]\)  \(R_1 = 0.0219, \ wR_2 = 0.0501\)  \(R_1 = 0.0538, wR_2 = 0.1354\)
\(R\) indices (all data)  \(R_1 = 0.0281, \ wR_2 = 0.0528\)  \(R_1 = 0.0775, wR_2 = 0.1486\)
Largest diff. peak and hole  0.364 and -0.498  1.319 and -1.664

**Table S4.** Data collection and structure refinement details for the compounds \(P_{\text{cin}3}\) and \(P_{\text{ind}1}\).

| Compound | \(P_{\text{cin}3}\) | \(P_{\text{ind}1}\) | \((\mu\text{-allyl})(\mu\text{-Cl})\text{Pd}_2(L2)_2\) |
|----------|----------------|----------------|------------------------------------------------|
| CCDC No. | 1952274 | 1952275 | 1978563 |
| Formula | \(\text{C}_{37}\text{H}_{63}\text{ClPd}_2\) | \(\text{C}_{53}\text{H}_{89}\text{ClO}_2\text{Pd}_2\) | \(\text{C}_{492}\text{H}_{822}\text{ClPd}_2\) |
| Formula weight [g·mol\(^{-1}\)] | 711.66 | 962.03 | 8970.23 |
| Temperature [K] | 100(2) | 100 (2) | 100 (2) |
| Wave length [Å] | 1.54184 | 1.54184 | 1.54184 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | \(P\overline{1}\) | \(P\overline{1}\) | \(P\overline{1}\) |
| \(a\) [Å] | 11.7098(4) | 10.6066(7) | 23.3437(4) |
| \(b\) [Å] | 12.0381(5) | 15.4445(8) | 23.8482(4) |
| \(c\) [Å] | 14.5289(3) | 16.6483(10) | 25.8949(2) |
| \(\alpha\) [°] | 78.495(3) | 84.749(5) | 94.4720(1) |
| \(\beta\) [°] | 82.349(2) | 71.902(5) | 95.4370(10) |
| \(\gamma\) [°] | 65.088(4) | 73.666(5) | 118.847(2) |
| Volume [Å\(^3\)] | 1817.39(12) | 2487.6(3) | 12443.1(4) |
| \(Z\) | 2 | 2 | 1 |
| Calc. density [Mg·m\(^{-3}\)] | 1.300 | 1.284 | 1.197 |
| \(\mu\) [mm\(^{-1}\)] | 5.785 | 4.363 | 4.804 |
| \(F(000)\) | 756 | 1032 | 4788 |
| Crystal dimensions [mm] | 0.073 x 0.054 x 0.024 | 0.123 x 0.021 x 0.013 | 0.106 x 0.085 x 0.044 |
| Theta range [°] | 3.109 to 77.484 | 2.792 to 67.183 | 2.552 to 77.502 |
| Index ranges | \(-14 \leq h \leq 14\) | \(-12 \leq h \leq 12\) | \(-29 \leq h \leq 26\) |
| | \(-13 \leq k \leq 15\) | \(-18 \leq k \leq 14\) | \(-30 \leq k \leq 30\) |
| | \(-18 \leq l \leq 18\) | \(-19 \leq l \leq 19\) | \(-32 \leq l \leq 32\) |
| Reflections collected | 7299 | 31897 | 84855 |
| Independent reflections | 7299 \([R_{int} = 0.0590]\) | 8795 \([R_{int} = 0.1473]\) | 8795 \([R_{int} = ?]\) |
| Data/Restraints/Parameter | 7299 / 0 / 377 | 8795 / 0 / 536 | 84855 / 0 / 2300 |
3.2 Crystal structures

3.2.1 Crystal Structure Determination of L2

![ORTEP Plot of L2](image)

**Figure S68** ORTEP Plot of L2. Ellipsoids are drawn at the 50% probability level.

**Table S5** Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for L2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

|   | x    | y    | z    | U(eq) |
|---|------|------|------|-------|
| P(1)| 6311(1)| 2504(1)| 4534(1)| 12(1) |
| P(2)| 8191(1)| 2472(1)| 3682(1)| 14(1) |
| C(1)| 6816(1)| 2399(1)| 3547(1)| 14(1) |
| C(2)| 6196(1)| 2504(1)| 2636(1)| 16(1) |
| C(3)| 6161(1)| 1913(1)| 1990(1)| 23(1) |
| C(4)| 5646(1)| 2006(1)| 1115(1)| 31(1) |
| C(5)| 5140(1)| 2694(1)| 859(1)| 33(1) |
| C(6)| 5154(1)| 3285(1)| 1487(1)| 28(1) |
| C(7)| 5676(1)| 3192(1)| 2362(1)| 21(1) |
| C(8)| 6838(1)| 1755(1)| 5356(1)| 15(1) |
| C(9)| 6711(1)| 919(1)| 5006(1)| 18(1) |
| C(10)| 7441(1)| 390(1)| 5623(1)| 21(1) |
| C(11)| 7223(1)| 431(1)| 6600(1)| 23(1) |
|       | U11   | U22   | U33   | U23   | U13   | U12   |
|-------|-------|-------|-------|-------|-------|-------|
| P(1)  | 12(1) | 13(1) | 12(1) | 0(1)  | 2(1)  | 0(1)  |
| P(2)  | 12(1) | 17(1) | 13(1) | 0(1)  | 2(1)  | 0(1)  |
| C(1)  | 13(1) | 17(1) | 12(1) | 0(1)  | 2(1)  | 0(1)  |
| C(2)  | 13(1) | 22(1) | 14(1) | 2(1)  | 3(1)  | -4(1) |
| C(3)  | 21(1) | 28(1) | 19(1) | -4(1) | 2(1)  | -3(1) |
| C(4)  | 29(1) | 44(1) | 17(1) | -7(1) | -1(1) | -9(1) |
| C(5)  | 27(1) | 53(1) | 17(1) | 5(1)  | -6(1) | -8(1) |
| C(6)  | 21(1) | 36(1) | 26(1) | 11(1) | -3(1) | -1(1) |
| C(7)  | 18(1) | 25(1) | 20(1) | 4(1)  | 2(1)  | -1(1) |
| C(8)  | 17(1) | 16(1) | 13(1) | 1(1)  | 2(1)  | 0(1)  |
| C(9)  | 21(1) | 15(1) | 18(1) | 0(1)  | 1(1)  | 0(1)  |
| C(10) | 22(1) | 18(1) | 23(1) | 2(1)  | 4(1)  | 3(1)  |
| C(11) | 22(1) | 22(1) | 24(1) | 9(1)  | 4(1)  | 4(1)  |
| C(12) | 28(1) | 26(1) | 17(1) | 4(1)  | 3(1)  | 2(1)  |

**Table S6** Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for L2. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [\text{h}^2 a^2 U_{11} + \ldots + 2\text{hka} b \cdot \text{U}^{12}]$. 
| C(13) | 24(1) | 19(1) | 16(1) | 2(1) | 6(1) | 2(1) |
|-------|-------|-------|-------|------|------|------|
| C(14) | 17(1) | 15(1) | 15(1) | 2(1) | 4(1) | -1(1) |
| C(15) | 16(1) | 18(1) | 21(1) | -4(1) | 2(1) | -2(1) |
| C(16) | 21(1) | 22(1) | 24(1) | -6(1) | 2(1) | -5(1) |
| C(17) | 33(1) | 18(1) | 33(1) | -6(1) | 5(1) | -7(1) |
| C(18) | 31(1) | 15(1) | 28(1) | -2(1) | 3(1) | 2(1) |
| C(19) | 23(1) | 16(1) | 19(1) | -1(1) | 3(1) | 1(1) |
| C(20) | 13(1) | 17(1) | 15(1) | 2(1) | 1(1) | -1(1) |
| C(21) | 16(1) | 27(1) | 21(1) | -3(1) | 5(1) | 0(1) |
| C(22) | 16(1) | 30(1) | 30(1) | 2(1) | 5(1) | 2(1) |
| C(23) | 13(1) | 30(1) | 40(1) | -2(1) | 5(1) | -3(1) |
| C(24) | 18(1) | 25(1) | 32(1) | -6(1) | -3(1) | -3(1) |
| C(25) | 17(1) | 18(1) | 27(1) | -4(1) | 2(1) | -2(1) |
| C(26) | 15(1) | 20(1) | 17(1) | -1(1) | 3(1) | 2(1) |
| C(27) | 15(1) | 25(1) | 23(1) | 0(1) | 5(1) | 1(1) |
| C(28) | 18(1) | 29(1) | 26(1) | 0(1) | 8(1) | 4(1) |
| C(29) | 23(1) | 25(1) | 39(1) | -2(1) | 12(1) | 7(1) |
| C(30) | 25(1) | 21(1) | 40(1) | -6(1) | 12(1) | 1(1) |
| C(31) | 19(1) | 20(1) | 26(1) | -1(1) | 8(1) | 2(1) |
| C(32) | 17(1) | 17(1) | 19(1) | 0(1) | 6(1) | -1(1) |
| C(33) | 25(1) | 22(1) | 19(1) | 2(1) | 6(1) | 0(1) |
| C(34) | 33(1) | 25(1) | 29(1) | 9(1) | 13(1) | 4(1) |
| C(35) | 36(1) | 24(1) | 44(1) | 7(1) | 20(1) | -3(1) |
| C(36) | 32(1) | 25(1) | 41(1) | -4(1) | 13(1) | -11(1) |
| C(37) | 23(1) | 27(1) | 27(1) | -2(1) | 4(1) | -9(1) |
3.2.2 Crystal Structure Determination of L2·AuCl

Figure S69 ORTEP Plot of L2·AuCl. Ellipsoids are drawn at the 50% probability level.

Table S7 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for L2·AuCl. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|        | x    | y    | z    | $U_{eq}$ |
|--------|------|------|------|----------|
| Au(1)  | 8242 | 6923 | 5164 | 13       |
| Cl(1)  | 10057| 7146 | 6443 | 19       |
| P(1)   | 8175 | 5405 | 2884 | 11       |
| P(2)   | 6522 | 6718 | 3879 | 12       |
| C(1)   | 6760 | 5976 | 2905 | 13       |
| C(2)   | 5699 | 5898 | 1949 | 15       |
| C(3)   | 5821 | 6212 | 930  | 18       |
| C(4)   | 4821 | 6139 | 69   | 22       |
| C(5)   | 3658 | 5756 | 211  | 24       |
| C(6)   | 3525 | 5436 | 1202 | 23       |
| C(7)   | 4526 | 5510 | 2067 | 19       |
| C(8)   | 7780 | 4573 | 1887 | 14       |
| C(9)   | 6885 | 3904 | 2252 | 20       |
| C(10)  | 6385 | 3328 | 1315 | 27       |
| C(11)  | 7500 | 2912 | 871  | 28       |
| C(12)  | 8442 | 3563 | 544  | 26       |
| C(13)  | 8938 | 4144 | 1481 | 20       |
| C(14)  | 8848 | 4980 | 4205 | 15       |
Table S8 Anisotropic displacement parameters (Å² x 10³) for L₂·AuCl. The anisotropic displacement factor exponent takes the form: –2π² [h²a²U₁₁ + ... + 2 h k a b U₁₂].

|     | U¹¹  | U²²  | U³³  | U¹²  | U¹³  | U²³  |
|-----|------|------|------|------|------|------|
| Au(1)| 12(1)| 15(1)| 12(1)| -1(1)| 1(1) | 0(1) |
| Cl(1)| 16(1)| 23(1)| 16(1)| -2(1)| -5(1)| -2(1)|
| C(3) | 17(2) | 19(2) | 15(2) | -3(2) | -2(2) | 3(2)  |
| C(4) | 21(2) | 23(2) | 19(2) | -3(2) | -4(2) | 4(2)  |
| C(5) | 17(2) | 26(2) | 26(2) | -6(2) | -7(2) | 6(2)  |
| C(6) | 14(2) | 27(3) | 27(2) | -4(2) | -1(2) | -2(2) |
| C(7) | 14(2) | 22(2) | 20(2) | -1(2) | 1(2)  | -1(2) |
| C(8) | 16(2) | 14(2) | 13(2) | -3(2) | 1(2)  | -1(2) |
| C(9) | 24(2) | 18(2) | 19(2) | -2(2) | 4(2)  | -9(2) |
| C(10) | 31(3) | 23(3) | 27(2) | -7(2) | 1(2)  | -14(2) |
| C(11) | 41(3) | 19(2) | 25(2) | -9(2) | 2(2)  | -7(2) |
| C(12) | 34(3) | 23(3) | 22(2) | -4(2) | 1(2)  | 3(2)  |
| C(13) | 14(2) | 15(2) | 15(2) | 2(2)  | 2(2)  | 3(2)  |
| C(14) | 16(2) | 24(2) | 19(2) | 6(2)  | 6(2)  | 4(2)  |
| C(15) | 15(2) | 30(3) | 26(2) | 10(2) | -2(2) | 1(2)  |
| C(16) | 22(2) | 30(3) | 20(2) | 10(2) | 3(2)  | 2(2)  |
| C(17) | 27(2) | 26(3) | 17(2) | 6(2)  | 9(2)  | 8(2)  |
| C(18) | 17(2) | 27(3) | 21(2) | 11(2) | 4(2)  | 3(2)  |
| C(19) | 12(2) | 13(2) | 16(2) | 3(2)  | 3(2)  | 0(2)  |
| C(20) | 15(2) | 13(2) | 18(2) | -1(2) | 1(2)  | -2(2) |
| C(21) | 13(2) | 23(2) | 15(2) | -2(2) | 3(1)  | -3(2) |
| C(22) | 18(2) | 21(2) | 20(2) | 4(2)  | 4(2)  | -6(2) |
| C(23) | 17(2) | 23(3) | 17(2) | 4(2)  | 5(1)  | -1(2) |
| C(24) | 13(2) | 17(2) | 15(2) | 2(2)  | 3(2)  | -2(2) |
| C(25) | 13(2) | 18(2) | 16(2) | -1(2) | 4(2)  | -1(2) |
| C(26) | 16(2) | 25(2) | 22(2) | 4(2)  | 5(2)  | 1(2)  |
| C(27) | 21(2) | 30(3) | 28(2) | 8(2)  | 10(2) | 1(2)  |
| C(28) | 28(3) | 39(3) | 25(2) | 6(2)  | 15(2) | 6(2)  |
| C(29) | 22(2) | 33(3) | 24(2) | -3(3) | 10(2) | 5(3)  |
| C(30) | 23(2) | 27(3) | 23(2) | -4(2) | 5(2)  | -2(2) |
| C(31) | 12(2) | 13(2) | 20(2) | 2(2)  | 2(2)  | -1(2) |
| C(32) | 14(2) | 16(2) | 22(2) | 7(2)  | -3(2) | 0(2)  |
| C(33) | 18(2) | 17(2) | 31(3) | 4(2)  | -1(2) | 4(2)  |
| C(34) | 24(2) | 26(3) | 29(2) | 11(2) | -3(2) | 0(2)  |
| C(35) | 18(2) | 18(2) | 23(2) | 2(2)  | 2(2)  | -3(2) |
| C(36) | 16(2) | 17(2) | 18(2) | 0(2)  | 5(2)  | 2(2)  |
| Cl11 | 55(1) | 62(1) | 64(1) | -20(1) | 25(1) | -8(1) |
| Cl21 | 67(1) | 47(1) | 59(1) | -4(1) | 10(1) | -2(1) |
| Cl12 | 78(5) | 55(5) | 38(4) | -4(3) | 9(3)  | -33(4) |
| Cl22 | 58(1) | 38(1) | 54(1) | -7(1) | 12(1) | 7(1)  |
| Cl22 | 62(1) | 68(1) | 46(1) | -4(1) | 5(1)  | 14(1) |
3.2.3 Crystal Structure Determination of P$_{a1}$

Figure S70 ORTEP Plot of P$_{a1}$. Ellipsoids are drawn at the 50% probability level.

Table S9 Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for P$_{a1}$. U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

|      | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| Pd(1)| 5024(1)| 3575(1)| 988(1) | 18(1) |
| Cl(1)| 6958(1)| 4304(1)| 1400(1)| 24(1) |
| P(1) | 6439(1)| 2095(1)| 2645(1)| 14(1) |
| P(2) | 5781(1)| 2133(1)| 1162(1)| 15(1) |
| C(1) | 6289(2)| 1643(1)| 1907(1)| 16(1) |
| C(2) | 6709(2)| 679(1)| 1886(1)| 18(1) |
| C(3) | 8085(2)| 2385(1)| 3042(1)| 17(1) |
| C(4) | 8622(2)| 3173(1)| 2730(1)| 19(1) |
| C(5) | 9974(2)| 3404(1)| 3071(1)| 22(1) |
| C(6) | 10870(2)| 2621(1)| 3082(1)| 26(1) |
**Table S10** Anisotropic displacement parameters (Å² x 10³) for Pₐ1. The anisotropic displacement factor exponent takes the form: -2π² [h²a²U¹¹ + ... + 2hkabU¹²].

|         | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹² |
|---------|-----|-----|-----|-----|-----|-----|
| Pd(1)   | 18(1)| 17(1)| 20(1)| 1(1)| 2(1)| 1(1) |
| Cl(1)   | 21(1)| 19(1)| 31(1)| -1(1)| 0(1)| -3(1)|
| P(1)    | 12(1)| 15(1)| 14(1)| -2(1)| 2(1)| -1(1)|
| P(2)    | 14(1)| 16(1)| 14(1)| 0(1)| 3(1)| 0(1)|
| C(1)    | 17(1)| 14(1)| 15(1)| -1(1)| 3(1)| 1(1)|
| C(2)    | 22(1)| 16(1)| 17(1)| -2(1)| 4(1)| 1(1)|
| C(3)    | 15(1)| 19(1)| 16(1)| -1(1)| 2(1)| -3(1)|
| C(4)  | 18(1) | 17(1) | 22(1) | 0(1)  | 2(1)  | -2(1) |
|-------|-------|-------|-------|-------|-------|-------|
| C(5)  | 17(1) | 23(1) | 25(1) | 1(1)  | 2(1)  | -5(1) |
| C(6)  | 15(1) | 28(1) | 36(1) | 4(1)  | 4(1)  | -3(1) |
| C(7)  | 17(1) | 26(1) | 34(1) | 9(1)  | 0(1)  | 0(1)  |
| C(8)  | 17(1) | 18(1) | 26(1) | 2(1)  | 2(1)  | 0(1)  |
| C(9)  | 17(1) | 17(1) | 16(1) | -2(1) | 4(1)  | -2(1) |
| C(10) | 24(1) | 23(1) | 16(1) | -2(1) | 4(1)  | -3(1) |
| C(11) | 26(1) | 28(1) | 16(1) | 1(1)  | 4(1)  | -2(1) |
| C(12) | 28(1) | 30(1) | 24(1) | 6(1)  | 8(1)  | -6(1) |
| C(13) | 24(1) | 25(1) | 25(1) | 2(1)  | 4(1)  | -9(1) |
| C(14) | 20(1) | 24(1) | 18(1) | 1(1)  | 2(1)  | -6(1) |
| C(15) | 17(1) | 18(1) | 17(1) | -1(1) | 3(1)  | 2(1)  |
| C(16) | 21(1) | 21(1) | 23(1) | -8(1) | 2(1)  | 0(1)  |
| C(17) | 27(1) | 20(1) | 33(1) | -7(1) | 8(1)  | 1(1)  |
| C(18) | 26(1) | 22(1) | 34(1) | -4(1) | 10(1) | 6(1)  |
| C(19) | 19(1) | 26(1) | 27(1) | 0(1)  | 4(1)  | 4(1)  |
| C(20) | 16(1) | 21(1) | 21(1) | -2(1) | 4(1)  | 0(1)  |
| C(21) | 18(1) | 21(1) | 18(1) | -1(1) | 6(1)  | -2(1) |
| C(22) | 19(1) | 25(1) | 22(1) | 0(1)  | 7(1)  | -2(1) |
| C(23) | 19(1) | 34(1) | 31(1) | 1(1)  | 10(1) | 0(1)  |
| C(24) | 29(1) | 37(1) | 37(1) | 3(1)  | 21(1) | -2(1) |
| C(25) | 38(1) | 33(1) | 24(1) | 4(1)  | 14(1) | -1(1) |
| C(26) | 24(1) | 28(1) | 22(1) | 6(1)  | 7(1)  | 0(1)  |
| C(27) | 18(1) | 20(1) | 16(1) | -2(1) | 1(1)  | -1(1) |
| C(28) | 22(1) | 26(1) | 16(1) | -4(1) | 3(1)  | 1(1)  |
| C(29) | 24(1) | 31(1) | 20(1) | -8(1) | -2(1) | 2(1)  |
| C(30) | 21(1) | 30(1) | 26(1) | -6(1) | -4(1) | -2(1) |
| C(31) | 21(1) | 25(1) | 28(1) | -2(1) | 2(1)  | -5(1) |
| C(32) | 19(1) | 22(1) | 18(1) | -1(1) | 2(1)  | -3(1) |
| C(33) | 18(1) | 30(1) | 35(1) | -1(1) | -4(1) | 3(1)  |
| C(34) | 26(1) | 33(1) | 38(1) | 8(1)  | -6(1) | 7(1)  |
| C(35) | 31(1) | 21(1) | 47(1) | 8(1)  | -2(1) | 7(1)  |
3.2.4 Crystal Structure Determination of $P_{a}3$

![ORTEP Plot of $P_{a}3$. Ellipsoids are drawn at the 50% probability level.](image)

**Figure S71** ORTEP Plot of $P_{a}3$. Ellipsoids are drawn at the 50% probability level.

**Table S11** Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $P_{a}3$. $U(eq)$ is defined as one third of the trace of the orthogonalized Uij tensor.

|      | x     | y     | z     | $U(eq)$ |
|------|-------|-------|-------|---------|
| Pd(1)| 7237(1)| 3108(1)| 4260(1)| 15(1)   |
| Cl(1)| 8320(1)| 3326(1)| 3382(1)| 25(1)   |
| P(1) | 5570(1)| 969(1) | 3124(1)| 12(1)   |
| P(2) | 4959(1)| 2790(1)| 3920(1)| 15(1)   |
| C(1) | 4594(2)| 1922(1)| 3375(1)| 16(1)   |
| C(2) | 3244(2)| 1996(2)| 3037(1)| 21(1)   |
| C(3) | 4619(2)| -216(1)| 3135(1)| 15(1)   |
| C(4) | 3861(2)| -441(1)| 3679(1)| 19(1)   |
| C(5) | 2962(2)| -1358(2)| 3588(1)| 23(1)   |
| C(6) | 3790(2)| -2259(2)| 3410(1)| 24(1)   |
| C(7) | 4577(2)| -2034(1)| 2875(1)| 22(1)   |
| C(8) | 5468(2)| -1115(1)| 2957(1)| 16(1)   |
| C(9) | 5943(2)| 1063(1)| 2350(1)| 14(1)   |
| C(10)| 4795(2)| 729(1) | 1934(1)| 18(1)   |
| C(11)| 5229(2)| 825(1) | 1317(1)| 19(1)   |
| C(12)| 5674(2)| 1877(2)| 1179(1)| 21(1)   |
| C(13)| 6820(2)| 2198(2)| 1585(1)| 22(1)   |
Table S12 Anisotropic displacement parameters (Å$^2 \times 10^3$) for Pd3. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 U^{11} + \ldots + 2hkabU^{12}]$.

|     | U$^{11}$ | U$^{22}$ | U$^{33}$ | U$^{12}$ | U$^{13}$ | U$^{23}$ |
|-----|----------|----------|----------|----------|----------|----------|
| Pd(1) | 15(1)    | 17(1)    | 13(1)    | -1(1)    | 0(1)     | 1(1)     |
| Cl(1) | 31(1)    | 28(1)    | 17(1)    | -3(1)    | 5(1)     | -12(1)   |
| P(1)  | 11(1)    | 13(1)    | 12(1)    | 1(1)     | -1(1)    | 1(1)     |
| P(2)  | 14(1)    | 15(1)    | 14(1)    | 0(1)     | 0(1)     | 3(1)     |
| C(1)  | 14(1)    | 18(1)    | 17(1)    | -1(1)    | -2(1)    | 3(1)     |
| C(2)  | 16(1)    | 23(1)    | 24(1)    | -2(1)    | -5(1)    | 5(1)     |
| C(3)  | 14(1)    | 16(1)    | 16(1)    | 1(1)     | 0(1)     | 1(1)     |
| C(4)  | 18(1)    | 20(1)    | 20(1)    | 2(1)     | 2(1)     | 1(1)     |
| C(5)  | 18(1)    | 22(1)    | 28(1)    | 6(1)     | 4(1)     | -3(1)    |
| C(6)  | 24(1)    | 18(1)    | 32(1)    | 4(1)     | 2(1)     | -4(1)    |
| C(7)  | 23(1)    | 18(1)    | 24(1)    | -3(1)    | -2(1)    | -2(1)    |
| C(8)  | 15(1)    | 16(1)    | 18(1)    | -2(1)    | 1(1)     | -1(1)    |
| C(9)  | 14(1)    | 17(1)    | 12(1)    | -1(1)    | -1(1)    | 0(1)     |
| C(10)| 16(1)    | 21(1)    | 16(1)    | 0(1)     | -3(1)    | -4(1)    |
| C(11)| 20(1)    | 21(1)    | 15(1)    | -2(1)    | -4(1)    | -4(1)    |
| C(12) | 23(1) | 24(1) | 14(1) | 4(1)  | -3(1) | -5(1) |
|-------|-------|-------|-------|-------|-------|-------|
| C(13) | 22(1) | 26(1) | 17(1) | 2(1)  | -3(1) | -10(1) |
| C(14) | 20(1) | 21(1) | 16(1) | 0(1)  | -1(1) | -5(1)  |
| C(15) | 12(1) | 16(1) | 16(1) | 1(1)  | -2(1) | 0(1)  |
| C(16) | 14(1) | 25(1) | 18(1) | -1(1) | 0(1)  | 2(1)  |
| C(17) | 14(1) | 31(1) | 26(1) | -1(1) | -2(1) | 1(1)  |
| C(18) | 18(1) | 27(1) | 27(1) | -2(1) | -9(1) | 4(1)  |
| C(19) | 23(1) | 25(1) | 18(1) | -1(1) | -6(1) | 3(1)  |
| C(20) | 17(1) | 22(1) | 15(1) | 2(1)  | -1(1) | 3(1)  |
| C(21) | 18(1) | 22(1) | 20(1) | -2(1) | 5(1)  | 1(1)  |
| C(22) | 25(1) | 29(1) | 24(1) | -7(1) | 6(1)  | 4(1)  |
| C(23) | 17(1) | 30(1) | 28(1) | -2(1) | 4(1)  | 1(1)  |
| C(24) | 22(1) | 26(1) | 19(1) | 2(1)  | 5(1)  | 0(1)  |
| C(25) | 23(1) | 16(1) | 22(1) | -1(1) | -3(1) | 6(1)  |
| C(26) | 26(1) | 26(1) | 36(1) | -2(1) | -7(1) | 12(1) |
| C(27) | 31(1) | 16(1) | 29(1) | -4(1) | -4(1) | 4(1)  |
| C(28) | 39(1) | 19(1) | 22(1) | 4(1)  | -2(1) | 6(1)  |
| C(29A)| 28(2) | 31(3) | 10(2) | -8(2) | 1(1)  | -3(2) |
| C(30A)| 28(2) | 26(2) | 12(1) | -4(1) | -10(1) | 3(2) |
| C(31A)| 13(3) | 31(5) | 19(2) | -3(3) | -6(2) | 0(3)  |
| C(29B)| 35(4) | 41(5) | 10(3) | -8(4) | -2(2) | 1(4)  |
| C(30B)| 33(3) | 34(4) | 17(3) | -10(2) | -13(2) | 6(3) |
| C(31B)| 20(5) | 32(8) | 28(4) | 2(6)  | -9(3) | 2(5)  |
3.2.5 Crystal Structure Determination of P\textsubscript{cin}2

**Figure S72** ORTEP Plot of P\textsubscript{cin}2. Ellipsoids are drawn at the 50% probability level.

**Table S13** Atomic coordinates (x 10\(^4\)) and equivalent isotropic displacement parameters (Å\(^2\) x 10\(^3\)) for P\textsubscript{cin}2. U(eq) is defined as one third of the trace of the orthogonalized U\(_{ij}\) tensor.

|       | x    | y    | z    | U(eq) |
|-------|------|------|------|-------|
| Pd(1) | 5242 | 6683 | 6151 | 31(1) |
| Cl(1) | 6243 | 5638 | 6018 | 42(1) |
| P(1)  | 8516 | 7858 | 6101 | 27(1) |
| P(2)  | 6712 | 7006 | 6561 | 26(1) |
| C(1)  | 8268 | 7283 | 6427 | 27(1) |
| C(2)  | 9438 | 6895 | 6532 | 26(1) |
| C(3)  | 9734 | 6272 | 6391 | 33(1) |
| C(4)  | 10842| 5925 | 6483 | 39(1) |
| C(5)  | 11665| 6182 | 6721 | 40(1) |
| C(6)  | 11390| 6793 | 6871 | 40(1) |
| C(7)  | 10295| 7140 | 6780 | 36(1) |
| C(8)  | 8807 | 7511 | 5671 | 33(1) |
| C(9)  | 10117| 7174 | 5614 | 38(1) |
| C(10) | 10245| 6966 | 5238 | 47(1) |
| C(11) | 9173 | 6496 | 5136 | 60(2) |
| C(12) | 7860 | 6805 | 5199 | 57(2) |
| C(13) | 7735 | 7020 | 5573 | 42(1) |
| C(14) | 9984 | 8349 | 6182 | 35(1) |
| C(15) | 10039| 8756 | 6515 | 40(1) |
| C(16) | 11429| 8963 | 6583 | 52(1) |
Table S14: Anisotropic displacement parameters (Å\(^2\) x 10\(^3\)) for Pd(1). The anisotropic displacement factor exponent takes the form: \(-2\pi^2 [h^2 a^2 U_{11} + \ldots + 2h k a b U_{12}]\).

|     | \(U_{11}\) | \(U_{22}\) | \(U_{33}\) | \(U_{12}\) | \(U_{13}\) |
|-----|-------------|-------------|-------------|-------------|-------------|
| Pd(1)| 26(1)       | 26(1)       | 42(1)       | -1(1)       | -6(1)       |
| Cl(1)| 43(1)       | 28(1)       | 53(1)       | -5(1)       | -8(1)       |
| P(1) | 20(1)       | 24(1)       | 37(1)       | -1(1)       | 2(1)        |
| P(2) | 20(1)       | 23(1)       | 34(1)       | -1(1)       | 1(1)        |
| C(1) | 22(2)       | 25(2)       | 35(2)       | -1(2)       | 4(2)        |
| C(2) | 18(2)       | 25(2)       | 36(2)       | -1(2)       | 0(2)        |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C(3) | 34(2) | 25(2) | 39(2) | -2(2) | 0(2) |
| C(4) | 37(3) | 32(2) | 48(3) | 1(2) | 5(2) |
| C(5) | 23(2) | 44(3) | 54(3) | 13(2) | 1(2) |
| C(6) | 26(2) | 49(3) | 45(3) | 2(2) | -5(2) |
| C(7) | 29(2) | 33(2) | 45(3) | -1(2) | 2(2) |
| C(8) | 25(2) | 35(2) | 40(2) | 2(2) | 8(2) |
| C(9) | 31(2) | 36(2) | 48(3) | 3(2) | 13(2) |
| C(10) | 44(3) | 50(3) | 48(3) | 1(2) | 21(2) |
| C(11) | 56(4) | 69(4) | 55(3) | -22(3) | 16(3) |
| C(12) | 48(3) | 70(4) | 53(3) | -25(3) | 7(3) |
| C(13) | 36(3) | 48(3) | 42(3) | -12(2) | 7(2) |
| C(14) | 22(2) | 29(2) | 54(3) | 7(2) | 1(2) |
| C(15) | 29(2) | 31(2) | 59(3) | -5(2) | 6(2) |
| C(16) | 31(3) | 37(3) | 88(4) | -8(3) | -12(3) |
| C(17) | 34(3) | 38(3) | 135(6) | 8(3) | -14(3) |
| C(18) | 37(3) | 39(3) | 102(5) | 22(3) | 8(3) |
| C(19) | 31(3) | 32(2) | 70(4) | 13(2) | 4(2) |
| C(20) | 23(2) | 27(2) | 36(2) | -3(2) | 2(2) |
| C(21) | 34(2) | 39(2) | 37(2) | 2(2) | 2(2) |
| C(22) | 32(2) | 43(3) | 37(2) | 3(2) | -6(2) |
| C(23) | 38(3) | 41(3) | 49(3) | 7(2) | -10(2) |
| C(24) | 34(2) | 29(2) | 46(3) | -3(2) | -2(2) |
| C(25) | 28(2) | 26(2) | 40(2) | -1(2) | 6(2) |
| C(26) | 21(2) | 19(2) | 38(2) | 1(2) | 0(2) |
| C(27) | 28(2) | 33(2) | 42(3) | -2(2) | -1(2) |
| C(28) | 38(3) | 25(2) | 44(3) | 3(2) | 2(2) |
| C(29) | 43(3) | 26(2) | 49(3) | 6(2) | -2(2) |
| C(30) | 31(2) | 32(2) | 47(3) | 2(2) | -4(2) |
| C(31) | 33(2) | 30(2) | 39(2) | 3(2) | 0(2) |
| C(32) | 26(2) | 24(2) | 39(2) | 1(2) | 4(2) |
| C(33) | 29(2) | 33(2) | 40(2) | -6(2) | 6(2) |
| C(34) | 33(3) | 40(3) | 53(3) | -4(2) | 11(2) |
| C(35) | 51(3) | 35(2) | 45(3) | -7(2) | 12(2) |
| C(36) | 46(3) | 28(2) | 44(3) | -5(2) | -2(2) |
| C(37) | 31(2) | 24(2) | 35(2) | -5(2) | -3(2) |
| C(38) | 34(3) | 40(3) | 68(4) | -1(2) | -11(2) |
| C(39) | 43(3) | 50(3) | 71(4) | -5(3) | -22(3) |
| C(40) | 37(3) | 62(4) | 65(4) | 1(3) | -6(3) |
| C(41) | 44(3) | 35(2) | 58(3) | 3(2) | -12(2) |
| C(42) | 54(3) | 47(3) | 59(3) | 9(2) | -9(3) |
3.2.6 Crystal Structure Determination of Pcin3

![ORTEP Plot of Pcin3. Elipsoids are drawn at the 50% probability level.](image)

**Figure S73** ORTEP Plot of Pcin3. Elipsoids are drawn at the 50% probability level.

**Table S15** Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for Pcin3. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor:

|          | x        | y        | z        | U(eq)   |
|----------|----------|----------|----------|---------|
| Pd(1)    | 4423(1)  | 2249(1)  | 1488(1)  | 24(1)   |
| Cl(1)    | 2794(1)  | 4244(1)  | 1045(1)  | 32(1)   |
| P(1)     | 3281(1)  | 3943(1)  | 3857(1)  | 22(1)   |
| P(2)     | 5588(1)  | 2744(1)  | 2453(1)  | 21(1)   |
| C(1)     | 4784(4)  | 3626(3)  | 3359(3)  | 24(1)   |
| C(2)     | 5407(4)  | 4315(4)  | 3743(3)  | 32(1)   |
| C(3)     | 3302(4)  | 3640(3)  | 5158(3)  | 26(1)   |
Table S16 Anisotropic displacement parameters (Å² x 10³) for \( P \text{c}n\overline{3} \). The anisotropic displacement factor exponent takes the form: \(-2\pi² [h²a\cdot U_{11} + \ldots + 2hkab\cdot U_{12}].\)

|     | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|-----|---------------|---------------|---------------|---------------|---------------|---------------|
| Pd(1) | 24(1)     | 22(1)     | 26(1)     | -10(1)        | -1(1)         | -8(1)         |
| Cl(1) | 31(1)     | 28(1)     | 34(1)     | -5(1)         | -5(1)     | -7(1)         |
|   | P(1) | P(2) | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | C(8) | C(9) | C(10) | C(11) | C(12) | C(13) | C(14) | C(15) | C(16) | C(17) | C(18) | C(19) | C(20) | C(21) | C(22) | C(23) | C(24) | C(25) | C(26) | C(27) | C(28) | C(29) | C(30) | C(31) | C(32) | C(33) | C(34) | C(35) | C(36) | C(37) |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
3.2.7 Crystal Structure Determination of $P_{\text{ind}1}$

Figure S74 ORTEP Plot of $P_{\text{ind}1}$. Ellipsoids are drawn at the 50% probability level.

Table S17 Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $P_{\text{ind}1}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|         | $x$     | $y$     | $z$     | $U(\text{eq})$ |
|---------|---------|---------|---------|---------------|
| Pd(1)   | 6583(1) | 3304(1) | 1921(1) | 36(1)         |
| Cl(1)   | 4502(2) | 2959(1) | 2073(1) | 45(1)         |
| P(1)    | 7210(2) | 667(1)  | 3000(1) | 37(1)         |
| P(2)    | 8062(2) | 1901(1) | 1422(1) | 34(1)         |
| C(1)    | 8165(6) | 878(4)  | 2010(4) | 33(1)         |
| C(2)    | 9168(7) | 50(4)   | 1503(5) | 42(2)         |
| C(3)    | 6413(7) | 1669(4) | 3675(4) | 42(2)         |
| C(4)    | 7476(8) | 1995(5) | 3934(5) | 46(2)         |
| C(5)    | 6774(9) | 2903(5) | 4406(5) | 58(2)         |
| C(6)    | 5552(9) | 2843(5) | 5170(5) | 60(2)         |
| C(7) | 4518(9) | 2502(5) | 4911(5) | 57(2) |
| C(8) | 5220(7) | 1587(5) | 4472(5) | 47(2) |
| C(9) | 8293(8) | -229(4) | 3493(5) | 44(2) |
| C(10) | 7625(8) | -472(5) | 4405(5) | 50(2) |
| C(11) | 8477(8) | -1334(5) | 4689(6) | 54(2) |
| C(12) | 9940(9) | -1274(5) | 4589(6) | 60(2) |
| C(13) | 10620(9) | -982(6) | 3692(6) | 63(2) |
| C(14) | 5761(7) | 179(4) | 3067(5) | 41(2) |
| C(15) | 4610(7) | 852(4) | 2797(5) | 42(2) |
| C(16) | 3404(7) | 470(5) | 2870(5) | 47(2) |
| C(17) | 3895(8) | -387(5) | 2336(5) | 50(2) |
| C(18) | 5021(8) | -1078(5) | 2609(5) | 52(2) |
| C(19) | 6242(7) | -692(4) | 2543(5) | 48(2) |
| C(20) | 7802(6) | 1678(4) | 415(4) | 35(2) |
| C(21) | 7648(7) | 2543(4) | -136(4) | 39(2) |
| C(22) | 9826(7) | 2082(4) | 1034(4) | 38(2) |
| C(23) | 10415(7) | 2046(4) | 1768(5) | 42(2) |
| C(24) | 11706(7) | 2388(5) | 1507(5) | 46(2) |
| C(25) | 12799(8) | 1853(5) | 771(5) | 55(2) |
| C(26) | 12234(8) | 1868(5) | 17(5) | 52(2) |
| C(27) | 10927(6) | 1526(4) | 283(5) | 42(2) |
| C(28) | 5713(7) | 4904(4) | 2172(5) | 43(2) |
| C(29) | 6833(7) | 4469(4) | 2480(5) | 47(2) |
| C(30) | 8006(7) | 4121(4) | 1771(5) | 43(2) |
| C(31) | 7696(7) | 4574(4) | 1017(4) | 40(2) |
| C(32) | 6268(7) | 5040(4) | 1262(4) | 39(2) |
| C(33) | 5719(8) | 5523(4) | 645(5) | 50(2) |
| C(34) | 6559(9) | 5566(5) | -190(5) | 56(2) |
| C(35) | 7958(9) | 5102(5) | -411(5) | 52(2) |
| C(36) | 8525(8) | 4598(4) | 195(5) | 48(2) |
| C(37) | 4298(8) | 5378(5) | 2735(5) | 50(2) |
| C(38) | 4049(10) | 5026(6) | 3641(6) | 65(2) |
| C(39) | 3106(8) | 5276(5) | 2415(6) | 55(2) |
| C(40) | 4201(9) | 6401(5) | 2730(6) | 61(2) |
| O11 | 643(8) | 5855(5) | 5151(5) | 89(2) |
A18 Anisotropic displacement parameters (Å² x 10³) for \( \text{Pind1} \). The anisotropic displacement factor exponent takes the form: \(-2π^2 [h^2a^2U^{11} + \ldots + 2hkabU^{12}]\).

|        | \(U^{11}\)  | \(U^{22}\)  | \(U^{33}\)  | \(U^{23}\)  | \(U^{13}\)  | \(U^{12}\)  |
|--------|-------------|-------------|-------------|-------------|-------------|-------------|
| Pd(1)  | 32(1)       | 32(1)       | 45(1)       | -10(1)      | -13(1)      | -6(1)       |
| Cl(1)  | 34(1)       | 38(1)       | 64(1)       | -8(1)       | -14(1)      | -10(1)      |
| P(1)   | 38(1)       | 38(1)       | 42(1)       | -4(1)       | -15(1)      | -15(1)      |
| P(2)   | 30(1)       | 34(1)       | 42(1)       | -7(1)       | -13(1)      | -9(1)       |
| C(1)   | 31(3)       | 34(3)       | 34(3)       | -1(3)       | -8(3)       | -9(3)       |
| C(2)   | 41(4)       | 37(3)       | 49(4)       | -4(3)       | -11(3)      | -11(3)      |
| C(3)   | 48(4)       | 43(3)       | 40(4)       | -4(3)       | -16(3)      | -16(3)      |
| C(4)   | 55(5)       | 52(4)       | 42(4)       | -3(3)       | -13(4)      | -30(4)      |
| C(5)   | 75(6)       | 55(4)       | 56(5)       | -13(4)      | -16(4)      | -34(4)      |
| C(6)   | 80(6)       | 50(4)       | 58(5)       | -15(4)      | -22(5)      | -23(4)      |
| C(7)   | 64(5)       | 57(4)       | 49(5)       | -18(4)      | -7(4)       | -22(4)      |
| C(8)   | 47(4)       | 48(4)       | 47(4)       | -11(3)      | -9(4)       | -20(3)      |
| C(9)   | 54(4)       | 45(3)       | 42(4)       | 0(3)        | -21(3)      | -23(3)      |
| C(10)  | 58(5)       | 46(4)       | 55(5)       | 3(3)        | -28(4)      | -18(4)      |
| C(11)  | 59(5)       | 46(4)       | 66(5)       | 3(4)        | -28(4)      | -21(4)      |
| C(12)  | 63(5)       | 57(4)       | 78(6)       | 10(4)       | -41(5)      | -22(4)      |
| C(13)  | 46(5)       | 64(5)       | 91(7)       | 16(5)       | -35(5)      | -20(4)      |
| C(14)  | 49(5)       | 61(4)       | 56(5)       | 9(4)        | -23(4)      | -29(4)      |
| C(15)  | 42(4)       | 33(3)       | 56(4)       | -5(3)       | -25(3)      | -11(3)      |
| C(16)  | 41(4)       | 42(3)       | 47(4)       | -4(3)       | -12(3)      | -16(3)      |
| C(17)  | 45(4)       | 48(4)       | 58(5)       | -6(3)       | -25(4)      | -18(3)      |
| C(18)  | 47(4)       | 53(4)       | 59(5)       | -11(4)      | -22(4)      | -17(3)      |
| C(19)  | 56(5)       | 46(4)       | 67(5)       | -5(4)       | -26(4)      | -23(4)      |
| C(20)  | 45(4)       | 38(3)       | 69(5)       | -9(3)       | -28(4)      | -12(3)      |
| C(21)  | 29(3)       | 40(3)       | 39(4)       | -8(3)       | -12(3)      | -8(3)       |
| C(22)  | 39(4)       | 36(3)       | 43(4)       | -9(3)       | -15(3)      | -6(3)       |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| C(23) | 42(4) | 38(3) | 42(4) | -3(3) | -13(3) | -8(3) |
| C(24) | 45(4) | 40(3) | 50(4) | -7(3) | -22(4) | -5(3) |
| C(25) | 39(4) | 36(3) | 43(4) | -8(3) | -12(3) | -10(3) |
| C(26) | 33(4) | 39(3) | 51(4) | -7(3) | -17(3) | -12(3) |
| C(27) | 35(4) | 36(3) | 41(4) | -6(3) | -11(3) | -8(3) |
| C(28) | 40(4) | 40(3) | 55(4) | -5(3) | -22(3) | -14(3) |
| C(29) | 33(4) | 50(4) | 60(5) | -9(3) | -19(4) | -9(3) |
| C(30) | 36(4) | 61(4) | 73(6) | -8(4) | -22(4) | -12(4) |
| C(31) | 37(4) | 60(4) | 59(5) | -12(4) | -10(4) | -12(3) |
| C(32) | 25(3) | 43(3) | 55(4) | -16(3) | -8(3) | -4(3) |
| C(33) | 50(4) | 39(3) | 46(4) | -4(3) | -18(4) | -16(3) |
| C(34) | 57(5) | 27(3) | 68(5) | -13(3) | -29(4) | -12(3) |
| C(35) | 37(4) | 34(3) | 63(5) | -9(3) | -13(3) | -17(3) |
| C(36) | 49(4) | 32(3) | 48(4) | 0(3) | -25(4) | -16(3) |
| C(37) | 45(4) | 28(3) | 50(4) | -1(3) | -25(3) | -6(3) |
| C(38) | 58(5) | 39(3) | 58(5) | -9(3) | -23(4) | -11(3) |
| C(39) | 74(6) | 53(4) | 51(5) | -3(4) | -28(4) | -22(4) |
| C(40) | 63(5) | 44(4) | 58(5) | 0(4) | -22(4) | -23(4) |
| C(41) | 44(4) | 42(3) | 60(5) | -7(3) | -10(4) | -20(3) |
| C(42) | 54(5) | 47(4) | 49(5) | -8(3) | -19(4) | -5(3) |
| C(43) | 68(6) | 60(5) | 57(5) | -9(4) | -14(5) | -5(4) |
| C(44) | 42(4) | 47(4) | 74(6) | -17(4) | -18(4) | 0(3) |
| C(45) | 61(5) | 49(4) | 72(6) | -24(4) | -25(5) | -3(4) |
| O11 | 98(6) | 84(4) | 89(5) | -13(4) | -35(5) | -18(4) |
| C11 | 83(8) | 59(5) | 102(8) | -2(5) | -38(6) | -10(5) |
| C21 | 79(7) | 74(6) | 87(8) | -7(6) | -27(6) | -1(5) |
| C31 | 106(9) | 86(6) | 67(7) | 2(5) | -31(6) | -36(6) |
| C41 | 108(9) | 71(6) | 100(9) | 0(6) | -54(7) | -16(6) |
| O12 | 105(6) | 157(7) | 79(5) | -1(5) | -31(5) | -65(6) |
| C12 | 63(7) | 105(8) | 103(9) | -8(7) | -16(6) | -41(6) |
| C22 | 168(15) | 290(20) | 94(10) | -93(13) | 51(10) | 171(17) |
| C32 | 112(9) | 97(7) | 86(8) | -26(6) | -17(7) | -50(7) |
| C42 | 75(7) | 97(7) | 76(7) | -10(6) | -18(6) | -31(6) |
### 3.2.8 Crystal Structure Determination of (μ-allyl)(μ-Cl)Pd₂(L₂)

**Figure S75** ORTEP Plot of (μ-allyl)(μ-Cl)Pd₂(L₂). Ellipsoids are drawn at the 50% probability level.

**Table S19** Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for (μ-allyl)(μ-Cl)Pd₂(L₂). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

|       | x    | y    | z    | U(eq) |
|-------|------|------|------|-------|
| Pd(1) | 3067(1) | 2133(1) | 1826(1) | 36(1) |
| Pd(2) | 3998(1) | 2087(1) | 2444(1) | 36(1) |
| Cl(1)  | 3014(1) | 1128(1) | 2003(1) | 56(1) |
| P(1)   | 2147(1) | 1160(1) | 393(1)  | 44(1) |
| P(2)   | 2099(1) | 1987(1) | 1357(1) | 36(1) |
| P(3)   | 3802(1) | 1179(1) | 3738(1) | 30(1) |
| P(4)   | 4726(1) | 1848(1) | 2921(1) | 33(1) |
| C(1)   | 1799(4) | 1568(4) | 699(4)  | 44(2) |
| C(2)   | 1244(5) | 1613(4) | 405(4)  | 51(2) |
| C(3)   | 1325(6) | 1920(4) | -43(4)  | 55(3) |
| C(4)   | 815(6)  | 1954(5) | -330(5) | 76(4) |
| C      |   |   |   |   |
|--------|---|---|---|---|
| C(5)   | 199(7) | 1698(6) | -160(6) | 83(4) |
| C(6)   | 97(6)  | 1393(5) | 303(6)  | 81(4) |
| C(7)   | 620(5) | 1347(5) | 566(5)  | 60(3) |
| C(8)   | 3042(5) | 1666(5) | 309(5)  | 63(3) |
| C(9)   | 3545(6) | 1885(8) | 779(6)  | 82(4) |
| C(10)  | 4237(5) | 2214(7) | 687(4)  | 70(3) |
| C(11)  | 4362(5) | 2772(8) | 389(5)  | 87(5) |
| C(12)  | 3156(4) | 2215(5) | 4(4)    | 54(2) |
| C(13)  | 1734(5) | 847(4)  | -294(4) | 48(2) |
| C(14)  | 1779(6) | 400(7)  | -1192(5)| 76(3) |
| C(15)  | 1030(6) | 10(6)   | -1304(4)| 73(3) |
| C(16)  | 711(5)  | 313(5)  | -973(4) | 64(3) |
| C(17)  | 976(5)  | 405(5)  | -389(4) | 50(2) |
| C(18)  | 2098(6) | 494(5)  | 730(4)  | 58(3) |
| C(19)  | 2528(9) | 184(7)  | 588(5)  | 85(4) |
| C(20)  | 2491(10)| -279(8) | 980(5)  | 100(6)|
| C(21)  | 1779(11)| -784(7) | 1036(6) | 114(7)|
| C(22)  | 1349(8) | -472(6) | 1149(5) | 85(4) |
| C(23)  | 1370(7) | -41(5)  | 736(4)  | 72(4) |
| C(24)  | 2151(4) | 2789(4) | 1343(4) | 43(2) |
| C(25)  | 2594(4) | 3176(4) | 964(3)  | 36(2) |
| C(26)  | 2747(5) | 3876(4) | 1049(4) | 48(2) |
| C(27)  | 2129(5) | 3932(4) | 989(4)  | 49(2) |
| C(28)  | 1657(5) | 3528(4) | 1356(4) | 48(2) |
| C(29)  | 1514(5) | 2833(4) | 1278(4) | 48(2) |
| C(30)  | 1462(4) | 1619(4) | 1799(4) | 48(2) |
| C(31)  | 1733(5) | 1992(4) | 2357(4) | 52(2) |
| C(32)  | 1241(6) | 1691(5) | 2738(5) | 64(3) |
| C(33)  | 1040(6) | 988(6)  | 2738(5) | 69(3) |
| C(34)  | 770(5)  | 599(5)  | 2188(5) | 60(3) |
| C(35)  | 1254(4) | 906(4)  | 1815(4) | 46(2) |
| C(36)  | 3606(5) | 3126(4) | 1991(5) | 59(3) |
| C(37)  | 4139(10)| 3059(7) | 2101(13)| 48(7) |
| C(38)  | 3986(14)| 3093(10)| 2380(16)| 37(7) |
| C(39A) | 4542(5) | 3072(4) | 2526(5) | 59(3) |
| C(39B) | 4549(4) | 1467(4) | 3503(3) | 35(2) |
| C(40)  | 5110(4) | 1458(4) | 3829(3) | 34(2) |
| C(41)  | 5369(4) | 1789(4) | 4341(4) | 41(2) |
| C(44) | 5869(4) | 1762(4) | 4641(4) | 45(2) |
|-------|---------|---------|---------|-------|
| C(45) | 6160(5) | 1420(5) | 4436(4) | 58(3) |
| C(46) | 5924(4) | 1095(5) | 3925(4) | 50(2) |
| C(47) | 5399(4) | 1109(4) | 3638(3) | 38(2) |
| C(48) | 3834(4) | 806(4)  | 4336(4) | 40(2) |
| C(49) | 3215(5) | 568(4)  | 4605(4) | 47(2) |
| C(50) | 3346(6) | 408(5)  | 5147(4) | 57(2) |
| C(51) | 3568(6) | -96(5)  | 5117(4) | 58(3) |
| C(52) | 4153(5) | 106(5)  | 4827(4) | 53(2) |
| C(53) | 4009(5) | 254(4)  | 4279(3) | 43(2) |
| C(54) | 3540(4) | 1770(4) | 3960(3) | 34(2) |
| C(55) | 4011(4) | 2287(4) | 4411(3) | 36(2) |
| C(56) | 3726(4) | 2713(5) | 4597(4) | 44(2) |
| C(57) | 3570(5) | 3019(4) | 4142(4) | 49(2) |
| C(58) | 3127(5) | 2523(5) | 3694(4) | 49(2) |
| C(59) | 3414(4) | 2102(4) | 3513(3) | 40(2) |
| C(60) | 3096(4) | 596(4)  | 3246(3) | 38(2) |
| C(61) | 2401(4) | 460(5)  | 3332(4) | 50(2) |
| C(62) | 1879(5) | 34(5)   | 2865(5) | 64(3) |
| C(63) | 1898(6) | -580(5) | 2706(4) | 72(4) |
| C(64) | 2579(7) | -449(4) | 2634(4) | 66(3) |
| C(65) | 3080(5) | -45(4)  | 3128(4) | 51(2) |
| C(66) | 4917(4) | 1373(4) | 2429(3) | 40(2) |
| C(67) | 4352(4) | 672(4)  | 2286(3) | 41(2) |
| C(68) | 4481(5) | 291(5)  | 1858(4) | 53(2) |
| C(69) | 4610(6) | 626(5)  | 1370(4) | 60(3) |
| C(70) | 5185(5) | 1315(5) | 1506(4) | 54(2) |
| C(71) | 5066(5) | 1709(4) | 1930(4) | 47(2) |
| C(72) | 5537(4) | 2608(4) | 3105(3) | 36(2) |
| C(73) | 5528(4) | 3056(4) | 3551(3) | 38(2) |
| C(74) | 6115(4) | 3724(4) | 3624(4) | 45(2) |
| C(75) | 6750(4) | 3693(4) | 3724(4) | 48(2) |
| C(76) | 6790(4) | 3255(4) | 3285(4) | 48(2) |
| C(77) | 6182(4) | 2577(4) | 3202(4) | 43(2) |
| Pd11  | 4078(1) | 7083(1) | 2296(1) | 42(1) |
| Pd21  | 3153(1) | 6175(1) | 2735(1) | 40(1) |
| Cl11  | 3095(1) | 7107(1) | 2493(1) | 59(1) |
| P11   | 3871(1) | 7738(1) | 930(1)  | 35(1) |
| P21   | 4815(1) | 7990(1) | 1959(1) | 38(1) |
| P31   | 2396(1) | 6302(1) | 4054(1) | 31(1) |
|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| P41   | 2206(1) | 5425(1) | 3028(1) | 36(1) |
| C11   | 4626(4) | 8186(4) | 1330(3) | 40(2) |
| C21   | 5182(5) | 8737(4) | 1136(4) | 46(2) |
| C31   | 5463(5) | 9374(4) | 1390(4) | 54(2) |
| C41   | 5997(6) | 9881(4) | 1224(6) | 71(3) |
| C51   | 6252(6) | 9769(5) | 787(6)  | 72(3) |
| C61   | 5974(5) | 9147(5) | 527(5)  | 62(3) |
| C71   | 5455(4) | 8643(5) | 706(4)  | 48(2) |
| C81   | 3894(4) | 8104(4) | 319(3)  | 40(2) |
| C91   | 4089(5) | 8824(4) | 363(4)  | 47(2) |
| C101  | 4225(5) | 9067(5) | -157(4) | 57(2) |
| C111  | 3630(6) | 8685(5) | -582(4) | 60(3) |
| C121  | 3395(6) | 7960(5) | -623(4) | 56(2) |
| C131  | 3272(5) | 7714(4) | -98(4)  | 50(2) |
| C141  | 3606(4) | 6889(4) | 682(3)  | 35(2) |
| C151  | 4076(4) | 6811(4) | 337(4)  | 40(2) |
| C161  | 3821(5) | 6118(4) | 112(4)  | 48(2) |
| C171  | 3678(5) | 5679(4) | 537(4)  | 54(2) |
| C181  | 3206(5) | 5752(4) | 864(4)  | 53(2) |
| C191  | 3478(5) | 6453(4) | 1104(4) | 43(2) |
| C201  | 3172(4) | 7683(4) | 1246(4) | 42(2) |
| C211  | 2467(5) | 7154(5) | 1000(4) | 52(2) |
| C221  | 1963(6) | 7129(7) | 1366(5) | 72(3) |
| C231  | 2022(7) | 7788(7) | 1477(6) | 86(5) |
| C241  | 2713(7) | 8303(6) | 1707(5) | 75(4) |
| C251  | 3198(5) | 8332(5) | 1340(4) | 53(2) |
| C261  | 5617(5) | 7984(4) | 1961(4) | 46(2) |
| C271  | 6265(5) | 8630(5) | 1991(4) | 53(2) |
| C281  | 6865(4) | 8530(5) | 2056(4) | 52(2) |
| C291  | 6805(5) | 8030(5) | 1614(5) | 57(3) |
| C301  | 6166(5) | 7404(5) | 1570(5) | 57(3) |
| C311  | 5572(5) | 7507(4) | 1503(4) | 47(2) |
| C321  | 5054(5) | 8673(5) | 2485(4) | 47(2) |
| C331  | 5301(5) | 8545(5) | 3003(4) | 53(2) |
| C341  | 5502(5) | 9114(5) | 3446(4) | 55(2) |
| C351  | 4928(5) | 9239(5) | 3503(4) | 53(2) |
| C361  | 4692(5) | 9383(5) | 2985(4) | 54(2) |
| C371  | 4496(4) | 8830(4) | 2542(4) | 43(2) |
| C381  | 4601(5) | 6600(5) | 2359(5) | 55(2) |
| C39A1 | 4232(11) | 6281(12) | 2710(12) | 44(7) |
| Symbol | C39B1 | C401 | C411 | C421 | C431 | C441 | C451 | C461 | C471 | C481 | C491 | C501 | C511 | C521 | C531 | C541 | C551 | C561 | C571 | C581 | C591 | C601 | C611 | C621 | C631 | C641 | C651 | C661 | C671 | C681 | C691 | C701 | C711 | C721 | C731 | C741 | C751 | C761 | C771 | Pd12 |
|--------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|        | 4009(17) | 6052(17) | 2366(17) | 68(11) | 3683(5) | 5698(5) | 2720(5) | 58(3) | 1966(4) | 5577(4) | 3640(3) | 36(2) | 1402(4) | 5012(4) | 3820(4) | 41(2) | 761(4) | 4719(5) | 3536(4) | 49(2) | 242(4) | 4193(5) | 3691(5) | 56(3) | 337(5) | 3953(5) | 4150(6) | 67(3) | 961(5) | 4234(5) | 4435(5) | 58(3) | 1490(4) | 4757(4) | 4272(4) | 43(2) | 1960(4) | 6251(4) | 4625(3) | 40(2) | 1223(4) | 6067(5) | 4509(4) | 47(2) | 902(5) | 5884(6) | 5007(4) | 59(3) | 1250(5) | 6444(6) | 5443(4) | 63(3) | 2001(5) | 6690(6) | 5556(4) | 54(2) | 2309(4) | 6843(5) | 5053(3) | 46(2) | 2515(4) | 7008(4) | 3731(3) | 35(2) | 1872(4) | 7026(4) | 3589(4) | 42(2) | 1974(5) | 7540(5) | 3243(4) | 52(2) | 2510(5) | 8203(5) | 3514(4) | 55(2) | 3150(5) | 8210(5) | 3674(4) | 53(2) | 3052(4) | 7680(4) | 4018(3) | 40(2) | 3241(4) | 6538(4) | 4367(3) | 36(2) | 3722(4) | 6669(5) | 3964(3) | 41(2) | 4430(4) | 6913(5) | 4224(4) | 54(2) | 4453(4) | 6431(6) | 4559(4) | 55(3) | 3984(4) | 6287(5) | 4951(4) | 47(2) | 3268(4) | 6039(4) | 4699(3) | 39(2) | 2218(4) | 4644(4) | 3035(4) | 43(2) | 1572(5) | 4005(4) | 2972(4) | 49(2) | 1700(5) | 3432(4) | 2922(4) | 47(2) | 2171(5) | 3481(5) | 3397(4) | 47(2) | 2816(5) | 4108(5) | 3476(4) | 50(2) | 2683(4) | 4681(4) | 3515(4) | 39(2) | 1520(4) | 5185(4) | 2470(3) | 41(2) | 1319(4) | 5708(4) | 2429(4) | 44(2) | 766(6) | 5505(6) | 1967(4) | 61(3) | 937(7) | 5317(6) | 1460(4) | 69(3) | 1144(7) | 4801(6) | 1495(4) | 71(4) | 1706(5) | 5026(5) | 1960(4) | 51(2) | 7924(1) | 5986(1) | 2542(1) | 41(1) |
|   |   |   |   |   |
|---|---|---|---|---|
| Pd22 | 7956(1) | 6923(1) | 3183(1) | 40(1) |
| C12 | 8940(1) | 6899(1) | 2997(1) | 59(1) |
| P12 | 8782(1) | 6094(1) | 1231(1) | 32(1) |
| P22 | 8091(1) | 5223(1) | 2064(1) | 34(1) |
| P32 | 8902(1) | 7618(1) | 4667(1) | 44(1) |
| P42 | 8178(1) | 7859(1) | 3710(1) | 43(1) |
| C12 | 8468(4) | 5368(4) | 1482(3) | 36(2) |
| C22 | 8461(4) | 4810(4) | 1171(4) | 40(2) |
| C32 | 8113(4) | 4548(4) | 665(4)  | 44(2) |
| C42 | 8138(4) | 4055(5) | 369(4)  | 53(2) |
| C52 | 8494(5) | 3771(5) | 578(6)  | 69(3) |
| C62 | 8829(5) | 4014(5) | 1088(5) | 62(3) |
| C72 | 8824(4) | 4528(4) | 1367(4) | 47(2) |
| C82 | 9416(4) | 6759(4) | 1718(3) | 40(2) |
| C92 | 10044(4) | 6691(5) | 1833(4) | 50(2) |
| C102 | 10469(4) | 7108(5) | 2333(5) | 57(3) |
| C112 | 10657(5) | 7798(5) | 2308(5) | 62(3) |
| C122 | 10077(5) | 7908(5) | 2149(4) | 57(3) |
| C132 | 9628(5) | 7457(4) | 1644(4) | 54(2) |
| C142 | 9139(4) | 6041(4) | 628(3)  | 38(2) |
| C152 | 9682(4) | 5852(5) | 671(4)  | 47(2) |
| C162 | 9828(5) | 5710(5) | 128(4)  | 56(3) |
| C172 | 10051(5) | 6296(6) | -165(5) | 59(3) |
| C182 | 9534(5) | 6512(5) | -193(4) | 54(2) |
| C192 | 9382(5) | 6646(4) | 349(4)  | 43(2) |
| C202 | 8203(4) | 6386(4) | 1017(3) | 38(2) |
| C212 | 7910(5) | 6560(5) | 1470(4) | 47(2) |
| C222 | 7489(6) | 6853(6) | 1277(4) | 61(3) |
| C232 | 6937(5) | 6384(6) | 846(5)  | 66(3) |
| C242 | 7203(5) | 6186(5) | 392(4)  | 50(2) |
| C252 | 7645(4) | 5901(5) | 576(4)  | 45(2) |
| C262 | 7287(4) | 4446(4) | 1897(4) | 42(2) |
| C272 | 6848(4) | 4477(4) | 1436(4) | 41(2) |
| C282 | 6144(4) | 3900(5) | 1357(4) | 50(2) |
| C292 | 6156(4) | 3272(4) | 1284(4) | 49(2) |
| C302 | 6592(4) | 3235(5) | 1729(4) | 52(2) |
| C312 | 7291(4) | 3808(4) | 1812(4) | 45(2) |
| C322 | 8552(4) | 4998(4) | 2555(3) | 42(2) |
| C332 | 8225(4) | 4860(5) | 3046(4) | 50(2) |
| C342 | 8598(5) | 4687(5) | 3471(4) | 57(3) |
|   |   |   |   |   |
|---|---|---|---|---|
| C352 | 9317(5) | 5213(5) | 3612(4) | 55(2) |
| C362 | 9650(5) | 5353(5) | 3124(4) | 53(2) |
| C372 | 9283(4) | 5525(4) | 2702(4) | 40(2) |
| C382 | 6909(5) | 5518(5) | 2453(5) | 59(3) |
| C39A | 6980(10) | 6132(15) | 2599(12) | 47(8) |
| C39B | 6944(8) | 5908(13) | 2868(13) | 56(8) |
| C402 | 8579(4) | 8057(4) | 4386(4) | 44(2) |
| C412 | 8596(4) | 8611(5) | 4709(5) | 54(3) |
| C422 | 8236(4) | 8518(5) | 5139(5) | 56(3) |
| C432 | 10065(6) | 8476(7) | 6405(5) | 76(4) |
| C452 | 9877(6) | 8874(6) | 6083(5) | 69(3) |
| C462 | 9772(4) | 8650(5) | 5497(4) | 55(3) |
| C472 | 9312(5) | 6753(5) | 4701(5) | 65(3) |
| C482 | 8312(5) | 6753(5) | 4701(5) | 65(3) |
| C492 | 8047(7) | 6320(6) | 4202(5) | 75(3) |
| C502 | 7626(7) | 5593(5) | 4273(5) | 76(4) |
| C512 | 7064(7) | 5523(6) | 4564(5) | 84(4) |
| C522 | 7286(6) | 5946(6) | 5077(5) | 73(3) |
| C532 | 7751(5) | 6663(5) | 5003(5) | 56(2) |
| C542 | 9557(5) | 7610(6) | 4343(4) | 56(3) |
| C552 | 10155(5) | 8274(7) | 4375(5) | 80(4) |
| C562 | 10599(6) | 8265(7) | 3974(5) | 82(4) |
| C572 | 10788(7) | 7727(8) | 4079(5) | 84(4) |
| C582 | 10223(6) | 7090(7) | 4081(5) | 76(4) |
| C612 | 9774(7) | 7105(7) | 4459(5) | 75(4) |
| C622 | 7386(4) | 7889(4) | 3705(4) | 47(2) |
| C632 | 6935(4) | 7430(4) | 4052(4) | 41(2) |
| C642 | 6240(4) | 7339(5) | 3937(4) | 48(2) |
| C652 | 6260(5) | 7984(5) | 4033(5) | 55(2) |
| C702 | 6734(5) | 8466(5) | 3706(5) | 57(3) |
| C712 | 7424(5) | 8548(5) | 3827(5) | 60(3) |
| C722 | 8630(4) | 8529(5) | 3317(5) | 59(3) |
| C732 | 8261(5) | 8374(6) | 2775(5) | 73(4) |
|       | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-------|--------|--------|--------|--------|--------|--------|
| Pd(1) | 38(1)  | 32(1)  | 35(1)  | 8(1)   | 0(1)   | 16(1)  |
| Pd(2) | 40(1)  | 31(1)  | 35(1)  | 4(1)   | -4(1)  | 17(1)  |
| Cl(1) | 59(1)  | 28(1)  | 60(1)  | 9(1)   | -24(1) | 12(1)  |
| P(1)  | 51(1)  | 32(1)  | 41(1)  | 1(1)   | -13(1) | 18(1)  |
| P(2)  | 36(1)  | 28(1)  | 41(1)  | 7(1)   | 0(1)   | 14(1)  |
| P(3)  | 36(1)  | 25(1)  | 30(1)  | 4(1)   | -2(1)  | 16(1)  |
| P(4)  | 36(1)  | 28(1)  | 33(1)  | 3(1)   | 0(1)   | 16(1)  |
| C(1)  | 51(5)  | 34(4)  | 41(5)  | 4(3)   | -5(4)  | 20(4)  |
| C(2)  | 59(5)  | 29(4)  | 54(6)  | 3(4)   | -14(4) | 18(4)  |
| C(3)  | 76(6)  | 30(4)  | 49(6)  | 0(4)   | -15(5) | 22(4)  |
| C(4)  | 79(8)  | 46(6)  | 81(8)  | 0(5)   | -40(7) | 25(6)  |
| C(5)  | 85(9)  | 48(6)  | 103(10)| -2(6)  | -47(8) | 35(6)  |
| C(6)  | 57(6)  | 40(5)  | 128(12)| -9(7)  | -30(7) | 20(5)  |
| C(7)  | 48(5)  | 40(5)  | 81(8)  | 1(5)   | -16(5)| 20(4)  |
| C(8)  | 47(5)  | 36(5)  | 96(9)  | 9(5)   | -14(5)| 17(4)  |
| C(9)  | 58(7)  | 110(11)| 78(9)  | 26(8)  | 6(6)  | 40(7)  |
| C(10)| 53(6)  | 120(11)| 42(6)  | 12(6)  | 0(5)  | 48(7)  |
| C(11)| 41(5)  | 135(13)| 65(8)  | 37(8)  | 16(5) | 22(7)  |
| C(12)| 58(7)  | 86(9)  | 85(9)  | 8(7)   | 19(6) | 26(6)  |
| C(13)| 44(5)  | 49(5)  | 66(7)  | 7(5)   | -1(4) | 23(4)  |
| C(14)| 58(5)  | 41(5)  | 38(5)  | 6(4)   | -3(4) | 21(4)  |
| C(15)| 74(7)  | 73(7)  | 46(6)  | 13(5)  | 3(5)  | 41(6)  |
| C(16)| 82(8)  | 88(9)  | 45(6)  | 5(6)   | 5(6)  | 34(7)  |
| C(17)| 94(8)  | 66(7)  | 36(5)  | 10(5)  | 2(5)  | 23(6)  |
| C(18)| 63(6)  | 50(6)  | 46(6)  | 11(5)  | -5(5) | 5(5)   |
| C(19)| 53(5)  | 40(5)  | 40(5)  | 2(4)   | -3(4) | 11(4)  |
| C(20)| 88(7)  | 36(5)  | 46(5)  | -6(4)  | -15(5)| 33(5)  |
| C(21)| 162(14)| 84(9)  | 49(7)  | 8(6)   | 12(7) | 93(10) |
| C(22)| 191(18)| 90(11) | 56(8)  | 5(7)   | -3(9) | 102(12)|
| C(23)| 220(20)| 57(8)  | 71(9)  | 3(7)   | -29(11)|86(11) |
| C(24)| 125(11)| 48(6)  | 57(7)  | 15(5)  | -10(7)| 26(7)  |
| C(25)| 110(9) | 31(5)  | 46(6)  | -1(4)  | -24(6)| 19(5)  |

Table S20 Anisotropic displacement parameters (Å² x 10³) for (μ-allyl)(μ-Cl)Pd₂(L²). The anisotropic displacement factor exponent takes the form: \(-2π²[h²a·U^{11} + ... + 2 h k a·b·U^{12}].\)
| C(26)  | 47(4) | 39(4) | 42(5) | 17(4) | 12(4) | 19(4) |
| C(27)  | 43(4) | 33(4) | 33(4) | 11(3) | 1(3)  | 19(3) |
| C(28)  | 54(5) | 36(4) | 50(5) | 5(4)  | 3(4)  | 20(4) |
| C(29)  | 62(5) | 33(4) | 55(6) | 13(4) | 7(4)  | 26(4) |
| C(30)  | 56(5) | 42(5) | 52(6) | 9(4)  | 5(4)  | 30(4) |
| C(31)  | 53(5) | 36(4) | 59(6) | 17(4) | 12(4) | 24(4) |
| C(32)  | 43(4) | 32(4) | 68(6) | 19(4) | 6(4)  | 18(4) |
| C(33)  | 59(5) | 34(4) | 56(6) | 11(4) | 17(5) | 14(4) |
| C(34)  | 77(7) | 53(6) | 68(7) | 18(5) | 38(6) | 29(5) |
| C(35)  | 75(7) | 58(7) | 67(8) | 21(6) | 30(6) | 21(6) |
| C(36)  | 51(5) | 40(5) | 80(8) | 26(5) | 10(5) | 14(4) |
| C(37)  | 44(4) | 28(4) | 55(6) | 7(4)  | 4(4)  | 9(3)  |
| C(38)  | 58(6) | 24(4) | 87(8) | 12(4) | -7(5) | 16(4) |
| C(39A)| 54(10)| 23(7) | 56(15)| 1(7)  | -21(9)| 17(6) |
| C(39B)| 56(14)| 19(10)| 31(16)| -5(9) | 2(11) | 16(9) |
| C(40)  | 59(5) | 24(4) | 86(8) | 18(4) | -9(5) | 14(4) |
| C(41)  | 35(4) | 30(4) | 42(5) | 5(3)  | -1(3) | 20(3) |
| C(42)  | 37(4) | 30(4) | 37(4) | 5(3)  | 2(3)  | 18(3) |
| C(43)  | 43(4) | 33(4) | 45(5) | 7(4)  | -1(4) | 19(3) |
| C(44)  | 48(5) | 27(4) | 53(5) | -1(4) | -17(4)| 18(3) |
| C(45)  | 53(5) | 43(5) | 73(7) | 4(5)  | -21(5)| 24(4) |
| C(46)  | 43(5) | 47(5) | 63(6) | 6(4)  | -4(4) | 28(4) |
| C(47)  | 39(4) | 34(4) | 41(5) | 6(3)  | 1(3)  | 20(3) |
| C(48)  | 43(4) | 31(4) | 46(5) | 8(3)  | 3(4)  | 18(3) |
| C(49)  | 62(5) | 43(5) | 47(5) | 24(4) | 16(4) | 30(4) |
| C(50)  | 84(7) | 60(6) | 48(6) | 20(5) | 20(5) | 49(6) |
| C(51)  | 90(7) | 53(6) | 49(6) | 21(5) | 10(5) | 46(6) |
| C(52)  | 70(6) | 45(5) | 55(6) | 20(4) | 8(5)  | 36(5) |
| C(53)  | 63(5) | 40(4) | 37(5) | 15(4) | 8(4)  | 32(4) |
| C(54)  | 35(4) | 27(3) | 34(4) | 2(3)  | -2(3) | 14(3) |
| C(55)  | 35(4) | 35(4) | 37(4) | 0(3)  | 1(3)  | 19(3) |
| C(56)  | 45(4) | 46(5) | 42(5) | -4(4) | 0(4)  | 26(4) |
| C(57)  | 61(5) | 41(5) | 59(6) | 7(4)  | 11(4) | 37(4) |
| C(58)  | 58(5) | 56(5) | 43(5) | 13(4) | 8(4)  | 36(5) |
| C(59)  | 50(5) | 38(4) | 39(5) | 11(4) | 5(4)  | 28(4) |
| C(60)  | 47(4) | 28(4) | 32(4) | 5(3)  | -2(3) | 14(3) |
| C(61)  | 37(4) | 49(5) | 50(6) | 11(4) | -3(4) | 11(4) |
| C(62)  | 49(5) | 38(5) | 67(7) | 10(5) | -6(5) | -6(4) |
| C(63)  | 88(8) | 37(5) | 40(5) | 10(4) | -14(5)| -4(5) |
| C(64)  | 128(10)| 22(4)| 36(5)| 2(4) | 4(6)| 29(5)|
| C(65) | 71(6) | 27(4) | 41(5) | 3(3) | 4(4) | 14(4) |
|------|-------|-------|-------|------|------|-------|
| C(66) | 44(4) | 40(4) | 35(4) | 2(3) | 4(3) | 20(4) |
| C(67) | 50(5) | 34(4) | 37(5) | 1(3) | 5(4) | 22(4) |
| C(68) | 68(6) | 42(5) | 47(6) | 4(4) | 11(4) | 25(4) |
| C(69) | 89(8) | 57(6) | 38(5) | -7(4) | 8(5) | 40(6) |
| C(70) | 71(6) | 52(6) | 41(5) | 2(4) | 13(4) | 30(5) |
| C(71) | 50(5) | 37(4) | 41(5) | 4(4) | 11(4) | 11(4) |
| C(72) | 45(4) | 26(4) | 34(4) | 2(3) | -1(3) | 15(3) |
| C(73) | 43(4) | 32(4) | 33(4) | 0(3) | 5(4) | 16(3) |
| C(74) | 49(5) | 36(4) | 39(5) | 0(4) | -2(4) | 14(4) |
| C(75) | 47(5) | 36(4) | 41(5) | 2(4) | -6(4) | 8(4) |
| C(76) | 44(5) | 43(5) | 43(5) | 6(4) | 3(4) | 12(4) |
| C(77) | 40(4) | 40(4) | 44(5) | -2(4) | -1(4) | 18(4) |
| Pd11 | 55(1) | 45(1) | 38(1) | 12(1) | 17(1) | 33(1) |
| Pd21 | 49(1) | 47(1) | 36(1) | 14(1) | 12(1) | 32(1) |
| Cl11 | 79(2) | 69(2) | 70(2) | 38(1) | 41(1) | 59(1) |
| P11  | 45(1) | 30(1) | 35(1) | 8(1) | 11(1) | 21(1) |
| P21  | 47(1) | 37(1) | 36(1) | 1(1) | 8(1) | 25(1) |
| P31  | 31(1) | 36(1) | 31(1) | 9(1) | 6(1) | 20(1) |
| P41  | 41(1) | 39(1) | 34(1) | 4(1) | 0(1) | 25(1) |
| C11  | 45(4) | 38(4) | 40(5) | 6(3) | 7(3) | 23(4) |
| C21  | 54(5) | 34(4) | 52(5) | 2(4) | 2(4) | 24(4) |
| C31  | 65(6) | 29(4) | 64(7) | 2(4) | 0(5) | 21(4) |
| C41  | 76(7) | 22(4) | 100(10) | 11(5) | -4(7) | 16(4) |
| C51  | 63(6) | 48(6) | 99(10) | 32(6) | 21(6) | 18(5) |
| C61  | 58(6) | 48(6) | 84(8) | 26(5) | 27(5) | 22(5) |
| C71  | 46(5) | 43(5) | 57(6) | 10(4) | 11(4) | 22(4) |
| C81  | 56(5) | 26(4) | 41(5) | 6(3) | 7(4) | 23(3) |
| C91  | 70(6) | 28(4) | 46(5) | 8(4) | 7(4) | 26(4) |
| C101 | 73(6) | 40(5) | 62(7) | 19(5) | 17(5) | 28(5) |
| C111 | 74(7) | 45(5) | 59(6) | 25(5) | 11(5) | 26(5) |
| C121 | 74(6) | 48(5) | 47(6) | 8(4) | 4(5) | 31(5) |
| C131 | 54(5) | 32(4) | 55(6) | 2(4) | 5(4) | 15(4) |
| C141 | 39(4) | 27(4) | 35(4) | 2(3) | 8(3) | 13(3) |
| C151 | 41(4) | 30(4) | 47(5) | -1(3) | 8(4) | 16(3) |
| C161 | 60(5) | 34(4) | 50(6) | 3(4) | 10(4) | 24(4) |
| C171 | 73(6) | 29(4) | 71(7) | 8(4) | 9(5) | 33(4) |
| C181 | 64(6) | 30(4) | 60(6) | 10(4) | 7(5) | 20(4) |
| C191 | 56(5) | 26(4) | 48(5) | 13(3) | 15(4) | 19(4) |
| C201 | 54(5) | 47(5) | 40(5) | 9(4) | 16(4) | 35(4) |
| C211 | 51(5) | 60(6) | 52(6) | 18(5) | 16(4) | 30(5) |
|------|-------|-------|-------|-------|-------|-------|
| C221 | 77(7) | 99(9) | 83(8) | 48(7) | 45(6) | 66(7) |
| C231 | 101(10)| 100(10)| 124(12)| 65(9) | 73(9) | 86(9) |
| C241 | 132(11)| 87(8) | 67(7) | 23(6) | 39(5) | 47(5) |
| C251 | 73(6) | 55(6) | 48(6) | 6(4)  | 9(4)  | 35(4) |
| C261 | 57(6) | 55(6) | 48(6) | 0(4)  | 9(4)  | 35(4) |
| C271 | 60(5) | 40(5) | 49(5) | 0(4)  | 9(4)  | 35(4) |
| C281 | 57(5) | 59(6) | 52(6) | 0(4)  | 9(4)  | 35(4) |
| C291 | 44(5) | 48(5) | 64(6) | 0(4)  | 9(4)  | 35(4) |
| C301 | 54(5) | 55(5) | 45(5) | 3(4)  | 7(4)  | 39(4) |
| C311 | 56(5) | 55(5) | 45(5) | 3(4)  | 7(4)  | 39(4) |
| C321 | 54(5) | 55(5) | 45(5) | 3(4)  | 7(4)  | 39(4) |
| C331 | 52(5) | 56(5) | 87(8) | 8(5)  | 16(5) | 33(5) |
| C341 | 69(6) | 64(6) | 39(5) | -9(4) | -2(4) | 44(5) |
| C351 | 59(5) | 58(6) | 44(5) | -10(4)| 5(4)  | 33(5) |
| C361 | 74(6) | 67(6) | 42(5) | -4(5) | 10(4) | 52(5) |
| C371 | 52(5) | 36(4) | 44(5) | -3(4) | 0(4)  | 26(4) |
| C381 | 59(6) | 40(5) | 76(7) | 19(5) | 15(5) | 32(4) |
| C39A1| 64(12)| 66(13)| 39(15)| 28(11)| 24(10)| 54(11)|
| C39B1| 94(19)| 90(20)| 70(20)| 52(18)| 53(18)| 71(18)|
| C401 | 56(5) | 48(5) | 87(8) | 8(5)  | 20(5) | 39(5) |
| C411 | 32(4) | 36(4) | 38(4) | 0(3)  | -1(3) | 18(3) |
| C421 | 33(4) | 40(4) | 52(5) | 6(4)  | 5(3)  | 20(3) |
| C431 | 41(4) | 53(5) | 55(6) | -2(4) | -2(4) | 28(4) |
| C441 | 38(4) | 43(5) | 83(8) | 8(5)  | 6(5)  | 19(4) |
| C451 | 45(5) | 45(5) | 118(11)| 29(6) | 37(6) | 20(4) |
| C461 | 56(6) | 57(6) | 78(7) | 36(5) | 35(5) | 33(5) |
| C471 | 44(4) | 49(5) | 47(5) | 12(4) | 10(4) | 30(4) |
| C481 | 35(4) | 45(4) | 44(5) | 8(4)  | 9(3)  | 24(3) |
| C491 | 30(4) | 56(5) | 57(6) | 4(4)  | 12(4) | 23(4) |
| C501 | 45(5) | 70(7) | 69(7) | 14(6) | 25(5) | 30(5) |
| C511 | 60(6) | 83(8) | 57(6) | 16(6) | 28(5) | 41(6) |
| C521 | 54(5) | 76(7) | 42(5) | 7(5)  | 14(4) | 39(5) |
| C531 | 43(4) | 64(6) | 37(5) | 5(4)  | 6(4)  | 30(4) |
| C541 | 42(4) | 31(4) | 32(4) | 6(3)  | 8(3)  | 19(3) |
| C551 | 48(4) | 44(5) | 40(5) | 2(4)  | -2(4) | 29(4) |
| C561 | 69(6) | 64(6) | 41(5) | 8(4)  | -1(4) | 47(5) |
| C571 | 73(6) | 49(5) | 62(6) | 19(5) | 16(5) | 42(5) |
| C581 | 59(5) | 55(6) | 51(6) | 16(5) | 16(4) | 31(5) |
| C591 | 44(4) | 34(4) | 43(5) | 9(3)  | 5(4)  | 19(3) |
|    |   |   |   |   |   |   |
|----|---|---|---|---|---|---|
| C601 | 33(4) | 46(4) | 32(4) | 8(3) | 5(3) | 22(3) |
| C611 | 38(4) | 49(5) | 36(4) | 6(4) | 8(3) | 21(4) |
| C621 | 33(4) | 62(6) | 66(7) | 4(5) | 9(4) | 24(4) |
| C631 | 36(4) | 75(7) | 51(6) | -6(5) | -7(4) | 30(5) |
| C641 | 43(4) | 55(5) | 37(5) | -1(4) | -3(4) | 24(4) |
| C651 | 37(4) | 46(5) | 37(4) | 4(4) | 3(3) | 25(4) |
| C661 | 51(4) | 48(5) | 38(4) | 6(4) | 3(3) | 26(4) |
| C671 | 50(4) | 38(5) | 51(6) | 8(4) | 1(4) | 30(4) |
| C681 | 50(4) | 56(5) | 47(5) | 12(4) | 4(4) | 36(4) |
| C691 | 53(4) | 38(5) | 51(6) | 8(4) | 1(4) | 37(4) |
| C701 | 35(4) | 36(4) | 50(5) | 15(4) | 3(3) | 22(3) |
| C711 | 52(5) | 37(4) | 40(5) | 5(3) | -5(4) | 28(4) |
| C721 | 50(5) | 51(5) | 39(5) | 4(4) | -7(4) | 35(4) |
| C731 | 81(7) | 76(7) | 47(6) | 0(5) | -15(5) | 61(6) |
| C741 | 105(9) | 89(8) | 42(6) | -5(5) | -22(6) | 77(8) |
| C751 | 109(9) | 81(8) | 47(6) | -17(6) | -20(6) | 74(8) |
| C761 | 75(6) | 52(5) | 41(5) | -3(4) | -7(4) | 47(5) |
| Pd12 | 36(1) | 50(1) | 36(1) | 4(1) | 5(1) | 22(1) |
| Pd22 | 38(1) | 49(1) | 39(1) | 11(1) | 11(1) | 24(1) |
| C12 | 34(1) | 71(2) | 59(1) | -15(1) | 8(1) | 21(1) |
| P12 | 30(1) | 34(1) | 34(1) | 3(1) | 3(1) | 18(1) |
| P22 | 31(1) | 33(1) | 36(1) | 5(1) | 3(1) | 15(1) |
| P32 | 40(1) | 40(1) | 55(1) | -3(1) | 3(1) | 23(1) |
| P42 | 39(1) | 40(1) | 59(1) | 17(1) | 19(1) | 23(1) |
| C12 | 29(3) | 35(4) | 43(5) | 3(3) | 1(3) | 17(3) |
| C22 | 33(4) | 35(4) | 52(5) | 9(4) | 10(3) | 17(3) |
| C32 | 39(4) | 39(4) | 49(5) | 4(4) | 13(4) | 16(4) |
| C42 | 44(5) | 47(5) | 66(7) | -11(5) | 10(4) | 22(4) |
| C52 | 47(5) | 46(6) | 109(10) | -9(6) | 19(6) | 21(4) |
| C62 | 56(6) | 50(6) | 92(9) | 10(6) | 16(6) | 35(5) |
| C72 | 49(5) | 39(4) | 60(6) | 3(4) | 7(4) | 28(4) |
| C82 | 44(4) | 38(4) | 36(4) | -1(3) | 8(3) | 18(3) |
| C92 | 42(4) | 44(5) | 58(6) | 3(4) | 0(4) | 18(4) |
| C102 | 37(4) | 45(5) | 73(7) | -2(5) | -3(4) | 10(4) |
| C112 | 51(5) | 56(6) | 65(7) | -8(5) | 4(5) | 19(5) |
| C122 | 58(6) | 42(5) | 63(7) | -2(5) | 24(5) | 17(4) |
| C132 | 69(6) | 25(4) | 51(6) | -3(4) | 12(5) | 10(4) |
| C142 | 40(4) | 42(4) | 37(4) | 4(3) | 6(3) | 25(4) |
| C152 | 43(4) | 48(5) | 61(6) | 11(4) | 15(4) | 30(4) |
|    |    |    |    |    |    |
|---|---|---|---|---|---|
| C162 | 56(5) | 56(6) | 75(7) | 13(5) | 27(5) | 40(5) |
| C172 | 58(6) | 70(7) | 60(6) | 11(5) | 28(5) | 37(5) |
| C182 | 63(6) | 58(6) | 52(6) | 11(5) | 17(5) | 35(5) |
| C192 | 53(5) | 41(4) | 47(5) | 10(4) | 15(4) | 31(4) |
| C202 | 42(4) | 38(4) | 41(5) | 4(3)  | 7(3)  | 26(4) |
| C212 | 59(5) | 57(5) | 47(5) | 11(4) | 17(4) | 44(5) |
| C222 | 75(7) | 80(7) | 62(7) | 20(6) | 32(5) | 60(6) |
| C232 | 64(6) | 96(9) | 75(8) | 25(6) | 19(6) | 65(7) |
| C242 | 56(5) | 64(6) | 46(5) | 18(5) | 7(4)  | 40(5) |
| C252 | 40(4) | 49(5) | 52(5) | 1(4)  | 2(4)  | 30(4) |
| C262 | 35(4) | 44(5) | 44(5) | 11(4) | 7(3)  | 16(3) |
| C272 | 33(4) | 42(4) | 44(5) | -1(4) | -1(3) | 17(3) |
| C282 | 35(4) | 55(6) | 47(5) | -3(4) | -2(4) | 15(4) |
| C292 | 40(4) | 43(5) | 43(5) | 2(4)  | -5(4) | 7(4)  |
| C302 | 48(5) | 46(5) | 53(6) | 8(4)  | 2(4)  | 17(4) |
| C312 | 45(4) | 27(4) | 56(6) | 8(4)  | 1(4)  | 13(3) |
| C322 | 37(4) | 38(4) | 41(5) | 5(4)  | -2(3) | 13(3) |
| C332 | 34(4) | 59(6) | 45(5) | 7(4)  | -2(4) | 16(4) |
| C342 | 59(6) | 59(6) | 52(6) | 23(5) | -1(5) | 28(5) |
| C352 | 55(5) | 67(6) | 46(5) | 11(5) | -7(4) | 34(5) |
| C362 | 45(5) | 59(6) | 54(6) | 14(5) | -5(4) | 26(4) |
| C372 | 37(4) | 39(4) | 43(5) | 9(4)  | -1(3) | 18(3) |
| C382 | 44(5) | 50(5) | 86(8) | 10(5) | 16(5) | 24(4) |
| C39A2 | 31(10) | 94(19) | 15(12) | 2(12) | 6(8)  | 32(11) |
| C39B2 | 34(8) | 90(16) | 39(14) | -10(12) | 14(8) | 28(9) |
| C402 | 41(5) | 52(6) | 110(10) | 9(6) | 18(5) | 25(4) |
| C412 | 39(4) | 38(4) | 59(6) | 5(4) | 13(4) | 23(4) |
| C422 | 39(4) | 41(5) | 86(8) | 0(5) | 11(5) | 23(4) |
| C432 | 36(4) | 48(5) | 79(8) | -8(5) | 13(4) | 18(4) |
| C442 | 45(5) | 59(7) | 115(11) | -23(7) | 19(6) | 22(5) |
| C452 | 64(7) | 52(7) | 167(16) | -24(8) | 26(9) | 26(6) |
| C462 | 72(8) | 37(6) | 167(16) | 1(7) | 32(9) | 24(5) |
| C472 | 50(5) | 42(5) | 119(11) | 9(6) | 20(6) | 26(4) |
| C482 | 40(4) | 49(5) | 64(6) | -3(5) | 7(4) | 24(4) |
| C492 | 56(6) | 61(7) | 81(8) | 10(6) | 15(5) | 29(5) |
| C502 | 79(8) | 93(9) | 61(7) | 20(7) | 28(6) | 48(7) |
| C512 | 66(7) | 100(10) | 58(7) | 7(7) | 12(6) | 38(7) |
| C522 | 61(6) | 72(7) | 63(7) | -8(6) | 14(5) | 25(6) |
| C532 | 36(4) | 52(6) | 61(6) | -5(5) | 8(4) | 12(4) |
| C542 | 57(6) | 46(6) | 92(9) | -5(6) | -2(6) | 29(5) |
|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| C552 | 109(10) | 51(6) | 64(8) | 22(6) | 15(7) | 36(6) |
| C562 | 109(10) | 44(6) | 55(7) | -4(5) | -13(7) | 27(6) |
| C572 | 98(9) | 63(7) | 64(8) | 6(6) | 18(7) | 20(7) |
| C582 | 74(7) | 61(7) | 75(8) | 11(6) | 7(6) | 26(6) |
| C592 | 55(5) | 38(5) | 70(7) | 8(5) | -1(5) | 22(4) |
| C602 | 58(5) | 91(8) | 42(5) | -9(5) | 1(4) | 57(6) |
| C612 | 43(5) | 123(11) | 63(7) | -19(7) | 7(5) | 39(6) |
| C622 | 59(6) | 105(10) | 73(8) | -8(7) | 30(6) | 35(7) |
| C632 | 80(8) | 135(13) | 69(8) | 1(8) | 18(6) | 79(9) |
| C642 | 79(8) | 103(10) | 74(8) | 5(7) | 6(6) | 69(8) |
| C652 | 99(9) | 111(10) | 58(7) | 7(7) | 4(6) | 88(9) |
| C662 | 38(4) | 46(5) | 64(6) | 25(4) | 18(4) | 23(4) |
| C672 | 39(4) | 39(4) | 47(5) | 12(4) | 16(4) | 18(3) |
| C682 | 45(5) | 53(5) | 54(6) | 19(4) | 19(4) | 27(4) |
| C692 | 42(5) | 57(6) | 76(7) | 18(5) | 19(5) | 30(4) |
| C702 | 49(5) | 68(6) | 75(7) | 33(6) | 28(5) | 39(5) |
| C712 | 51(5) | 51(5) | 100(9) | 31(6) | 37(5) | 36(5) |
| C722 | 38(5) | 49(5) | 97(9) | 28(5) | 21(5) | 23(4) |
| C732 | 50(5) | 90(8) | 101(10) | 64(8) | 36(6) | 42(6) |
| C742 | 74(8) | 100(11) | 145(15) | 86(11) | 49(9) | 50(8) |
| C752 | 74(8) | 99(10) | 122(12) | 75(10) | 50(8) | 51(7) |
| C762 | 51(6) | 71(8) | 123(12) | 43(8) | 35(7) | 29(6) |
| C772 | 43(5) | 55(6) | 89(8) | 35(6) | 31(5) | 27(4) |
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