Supporting Information

for

Amido Pincer Complexes of Palladium: Synthesis, Structure, and Catalytic Heck Reaction

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1. **Figure S1.** The Hammett plot for the competitive reactions of aryl bromides with styrene
2. X-ray crystallographic report of [PNP]PdCl

1. The Hammett plot

Figure S1. Hammett plot for the coupling of aryl bromides (92 mM) with styrene catalyzed by **3a** (0.92 mM) in NMP at 160 °C, providing the reaction constant $\rho = 0.6034$.

2. X-ray crystallographic report of [PNP]PdCl

Abstract

We present the crystal and molecular structure of [PNP]PdCl.

Comment

The study of the titled structure was undertaken to establish its three dimensional structure. Geometries are tabulated below. All diagrams and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan).

Size: 0.12 x 0.10 x 0.07

Experimental

Crystal data

C₃₆H₂₈ClNP₂Pd

C₃₆H₂₈ClNP₂Pd

M_r = 678.428

Orthorhombic

Fdd2

a = 18.5222 (8) Å

b = 32.877 (2) Å

c = 9.9178 (4) Å

α = 90.00°

β = 90.00°

γ = 90.00°

V = 6039.5 (5) Å³

Z = 8

D_x = 1.492 Mg m⁻³

Density measured by: not measured
fine-focus sealed tube

Mo Kα radiation

λ = 0.71073

Cell parameters from 7804

θ = 2.037–25.028 °

μ = 0.836 mm⁻¹

T = 298 K

Cube

black

Crystal source: Local laboratory

fullmatrix least squares refinement

R(all) = 0.0583

R(gt) = 0.0410

wR(ref) = 0.1531

wR(gt) = 0.1099

S(ref) = 1.117

2399 reflections

182 parameters

1 restraints

Only coordinates of H atoms refined

Calculated weights calc

Δ/σ_{max} = 0.001

Δρ_{max} = 0.587 e Å⁻³

Δρ_{min} = -1.237 e Å⁻³

Extinction correction: none

Atomic scattering factors from International

Tables Vol C Tables 4.2.6.8 and 6.1.1.4

Flack parameter = -0.02 (6)

Flack H D (1983), *Acta Cryst.* A39, 876–881

Data collection: KappaCCD

Cell refinement: HKL Scalepack (Otwinowski & Minor 1997)

Data reduction: Denzo and Scalepak (Otwinowski & Minor, 1997)

Program(s) used to solve structure: *SIR92*

(Altomare et al., 1994)

Program(s) used to refine structure: *SHELXL-97*

(Sheldrick, 1997)

Data collection

KappaCCD

CCD

Absorption correction: multi-scan

T_{min} = 0.860, T_{max} = 0.923

5939 measured reflections

2399 independent reflections

2115 observed reflections

Criterion: >2σ(I)

θ_{max} = 24.98 °

h = -22 → 18

k = -31 → 38

l = -11 → 9

Refinement

Refinement on F²

Table . *Fractional atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2$)*

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}	Occ
Pd1	0.0000	0.0000	0.83279 (7)	0.0401 (3)	1
Cl1	0.0000	0.0000	1.0660 (5)	0.0823 (16)	1
P1	0.07221 (9)	0.05624 (6)	0.8030 (2)	0.0400 (5)	1
N1	0.0000	0.0000	0.6255 (11)	0.038 (3)	1
C1	0.1692 (4)	0.0464 (2)	0.7946 (9)	0.0419 (17)	1
C2	0.2126 (5)	0.0475 (3)	0.9091 (11)	0.057 (2)	1
C3	0.2856 (5)	0.0382 (3)	0.8996 (12)	0.063 (3)	1
C4	0.3142 (5)	0.0277 (3)	0.7795 (12)	0.066 (3)	1
C5	0.2731 (5)	0.0268 (3)	0.6668 (12)	0.066 (3)	1
C6	0.2004 (4)	0.0366 (3)	0.6717 (10)	0.051 (2)	1
C7	0.0477 (3)	0.0682 (2)	0.6309 (8)	0.0411 (18)	1
C8	0.0137 (4)	0.0369 (2)	0.5606 (8)	0.0395 (18)	1
C9	-0.0077 (4)	0.0452 (3)	0.4260 (10)	0.054 (2)	1
C10	0.0072 (5)	0.0824 (3)	0.3681 (9)	0.062 (3)	1
C11	0.0431 (5)	0.1121 (3)	0.4378 (11)	0.061 (2)	1
C12	0.0624 (4)	0.1055 (2)	0.5704 (9)	0.0474 (18)	1
C13	0.0604 (4)	0.1022 (2)	0.9022 (8)	0.0440 (18)	1
C14	0.1126 (4)	0.1326 (3)	0.9080 (9)	0.052 (2)	1
C15	0.0993 (5)	0.1677 (3)	0.9765 (10)	0.059 (2)	1
C16	0.0340 (5)	0.1740 (3)	1.0384 (10)	0.065 (2)	1
C17	-0.0188 (6)	0.1439 (3)	1.0353 (11)	0.072 (3)	1
C18	-0.0053 (5)	0.1084 (3)	0.9681 (11)	0.058 (2)	1
H2	0.1913	0.0551	0.9937	0.069	1
H3	0.3163	0.0371	0.9774	0.075	1
H4	0.3647	0.0218	0.7701	0.079	1
H5	0.2945	0.0202	0.5814	0.079	1
H6	0.1706	0.0359	0.5925	0.062	1
H9	-0.0329	0.0240	0.3788	0.065	1
H10	-0.0070	0.0879	0.2768	0.074	1
H11	0.0553	0.1374	0.3955	0.073	1
H12	0.0860	0.1265	0.6215	0.057	1
H14	0.1581	0.1290	0.8632	0.063	1
H15	0.1356	0.1885	0.9822	0.070	1
H16	0.0233	0.1988	1.0854	0.078	1
H17	-0.0638	0.1485	1.0807	0.087	1
H18	-0.0410	0.0873	0.9629	0.069	1

Table . *Anisotropic displacement parameters ($\text{\AA}^2$)*

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
Pd1	0.0455 (4)	-0.0059 (4)	0.000	0.0374 (4)	0.000	0.0375 (4)
Cl1	0.138 (5)	-0.0151 (17)	0.000	0.064 (3)	0.000	0.044 (3)
N1	0.048 (6)	-0.008 (4)	0.000	0.047 (6)	0.000	0.019 (5)
C1	0.042 (4)	0.001 (3)	-0.004 (3)	0.033 (3)	-0.002 (3)	0.051 (5)
C2	0.060 (5)	0.000 (4)	-0.010 (4)	0.055 (5)	-0.007 (4)	0.057 (6)
C3	0.055 (5)	0.006 (4)	-0.028 (5)	0.056 (6)	0.001 (5)	0.076 (7)
C4	0.046 (5)	0.007 (5)	-0.008 (5)	0.065 (6)	-0.007 (5)	0.087 (8)
C5	0.051 (4)	0.011 (5)	0.007 (5)	0.064 (6)	-0.018 (6)	0.082 (8)
C6	0.043 (4)	0.007 (4)	-0.009 (4)	0.050 (5)	-0.004 (4)	0.062 (6)
C7	0.029 (3)	-0.002 (3)	-0.002 (3)	0.048 (4)	0.008 (3)	0.046 (5)
C8	0.032 (3)	0.002 (3)	-0.001 (3)	0.048 (4)	0.013 (4)	0.038 (5)
C9	0.052 (5)	-0.008 (4)	-0.011 (4)	0.061 (5)	0.004 (4)	0.050 (6)
C10	0.072 (6)	0.012 (5)	-0.003 (4)	0.070 (6)	0.012 (4)	0.044 (7)
C11	0.067 (5)	0.003 (4)	0.010 (5)	0.046 (5)	0.020 (5)	0.071 (7)

C12	0.047 (4)	0.002 (3)	0.008 (4)	0.042 (4)	0.005 (4)	0.053 (5)
C13	0.047 (4)	0.000 (3)	-0.001 (3)	0.041 (4)	0.002 (3)	0.044 (5)
C14	0.051 (4)	-0.003 (4)	0.002 (4)	0.044 (5)	-0.005 (4)	0.061 (6)
C15	0.064 (5)	-0.003 (4)	-0.003 (4)	0.046 (5)	-0.017 (4)	0.065 (6)
C16	0.087 (6)	0.004 (5)	0.006 (5)	0.044 (5)	-0.013 (5)	0.064 (7)
C17	0.076 (5)	0.013 (5)	0.029 (5)	0.070 (7)	-0.009 (6)	0.071 (7)
C18	0.057 (5)	-0.004 (4)	0.006 (4)	0.050 (5)	-0.002 (5)	0.066 (7)

Table . *Geometric parameters* (Å, °)

Pd1-N1	2.056 (11)
Pd1-P1 ⁱ	2.3009 (18)
Pd1-P1	2.3010 (18)
Pd1-Cl1	2.313 (5)
P1-C7	1.810 (8)
P1-C13	1.816 (8)
P1-C1	1.828 (7)
N1-C8	1.396 (9)
N1-C8 ⁱ	1.396 (9)
C1-C6	1.387 (12)
C1-C2	1.392 (12)
C2-C3	1.389 (14)
C3-C4	1.349 (16)
C4-C5	1.353 (14)
C5-C6	1.385 (12)
C7-C12	1.392 (11)
C7-C8	1.393 (11)
C8-C9	1.420 (13)
C9-C10	1.378 (14)
C10-C11	1.368 (14)
C11-C12	1.381 (14)
C13-C14	1.392 (11)
C13-C18	1.397 (11)
C14-C15	1.361 (12)
C15-C16	1.372 (14)
C16-C17	1.390 (15)
C17-C18	1.367 (14)
C2-H2	0.9603
C3-H3	0.9592
C4-H4	0.9598
C5-H5	0.9600
C6-H6	0.9603
C9-H9	0.9606
C10-H10	0.9601
C11-H11	0.9586
C12-H12	0.9616
C14-H14	0.9600
C15-H15	0.9607
C16-H16	0.9599
C17-H17	0.9593
C18-H18	0.9597
N1-Pd1-P1 ⁱ	82.63 (6)
N1-Pd1-P1	82.63 (6)
P1 ⁱ -Pd1-P1	165.27 (11)
N1-Pd1-Cl1	180.0000 (10)
P1 ⁱ -Pd1-Cl1	97.37 (6)
P1-Pd1-Cl1	97.37 (6)
C7-P1-C13	107.4 (4)
C7-P1-C1	104.0 (4)

C13-P1-C1	106.9 (3)
C7-P1-Pd1	98.6 (2)
C13-P1-Pd1	122.0 (3)
C1-P1-Pd1	115.8 (2)
C8-N1-C8 ⁱ	125.2 (10)
C8-N1-Pd1	117.4 (5)
C8 ⁱ -N1-Pd1	117.4 (5)
C6-C1-C2	118.9 (8)
C6-C1-P1	119.4 (6)
C2-C1-P1	121.7 (7)
C3-C2-C1	120.1 (9)
C4-C3-C2	119.9 (9)
C3-C4-C5	121.0 (8)
C4-C5-C6	120.9 (9)
C5-C6-C1	119.3 (8)
C12-C7-C8	121.6 (7)
C12-C7-P1	123.3 (6)
C8-C7-P1	115.1 (6)
C7-C8-N1	119.6 (7)
C7-C8-C9	117.0 (7)
N1-C8-C9	123.3 (8)
C10-C9-C8	120.5 (8)
C11-C10-C9	121.3 (8)
C10-C11-C12	119.8 (8)
C11-C12-C7	119.8 (8)
C14-C13-C18	118.8 (8)
C14-C13-P1	122.4 (6)
C18-C13-P1	118.7 (6)
C15-C14-C13	120.2 (8)
C14-C15-C16	120.7 (9)
C15-C16-C17	120.2 (9)
C18-C17-C16	119.4 (9)
C17-C18-C13	120.7 (9)
C3-C2-H2	121.1
C1-C2-H2	118.8
C4-C3-H3	117.9
C2-C3-H3	122.0
C3-C4-H4	121.3
C5-C4-H4	117.6
C4-C5-H5	120.1
C6-C5-H5	119.0
C5-C6-H6	121.6
C1-C6-H6	119.0
C10-C9-H9	122.5
C8-C9-H9	117.0
C11-C10-H10	118.4
C9-C10-H10	120.4
C10-C11-H11	120.8
C12-C11-H11	119.4
C11-C12-H12	120.5
C7-C12-H12	119.6
C15-C14-H14	119.6
C13-C14-H14	120.1
C14-C15-H15	120.4
C16-C15-H15	118.9
C15-C16-H16	121.8
C17-C16-H16	118.0
C18-C17-H17	121.4
C16-C17-H17	119.2
C17-C18-H18	121.2

C13-C18-H18 118.0
Symmetry codes: (i) $x, 1/2+y, 1/2+z$.

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