Phosphido Pincer Complexes of Palladium as new Efficient Catalysts for Allylation of Aldehydes

Mina Mazzeo,* Marina Lamberti, Antonio Massa, Arrigo Scettri, Claudio Pellecchia, Jonas C. Peters[‡]

Dipartimento di Chimica, Università di Salerno, Via Ponte don Melillo, I-84084 Fisciano, Salerno, Italy

[‡]Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Fax: +39 089 969603; Tel: +39 089 969566.

E-mail: mmazzeo@unisa.it

Supporting information

(Fully-labelled drawings, crystal data and refinement, atomic coordinates and displacement parameters, bond lengths and angles, anisotropic parameters, and hydrogen coordinates and displacement)

I. Experimental section

General Remarks: All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen atmosphere using a Braun Labmaster drybox or standard Schlenk line techniques. All used solvents were refluxed over sodium-benzophenone and distilled under a nitrogen atmosphere before use.

Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and degassed and dried over activated 3 Å molecular sieves prior to use.

Bruker Avance spectrometers were used to record ^{1}H (400 and 300 MHz), ^{13}C (100.6 MHz), and ^{31}P NMR (161.97 MHz) spectra at ambient temperature. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane and coupling constants (J) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ7.16 for C_6D_6 and δ7.27 for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ128.39 for C_6D_6 and δ77.23 for $CDCl_3$. The ^{31}P NMR spectra are referenced externally using 85% H_3PO_4 at δ0. Elemental analyses of complex 1 were performed by Desert Analytics, Tucson, AZ. For complex 2 the elemental analyses were recorded on Thermo Finnigan Flash EA 1112 series, C, H, N, S Analyzer.

Synthesis of (iPr-PPP)PdCl (1): To a suspension of $(COD)PdCl_2$ (0.478 g; 1.67 mmol) and the iPr- PPP-H ligand (0.700 g; 1.67 mmol) in THF (15mL), was quickly added at room temperature, a solution of NEt^iPr_2 (0.308g, 2.38 mmol) in 2 mL of THF. The slurry was stirred at 50 °C for 2 h. The resulting orange solution was cooled at room temperature and the volatiles evaporated in vacuo. The crude orange product was extracted with benzene (~15 mL) and the resulting solution was filtered through celite on a sintered-glass frit. The solvent was eliminated in vacuo and the resulting orange solid was washed with petroleum ether (2× 5 mL) obtaining an analytical pure product (yield 0.720 g, 78%) .

^{1}H NMR (300 MHz; benzene-d_6) δ = 7.89 (dd, 2 H, Ar-*H*, $^2J_{P-H}$ = 8Hz, $^1J_{H-H}$ = 3Hz), 7.09 (t, 2H, Ar-*H*), 7.02 (b, 2H, Ar-*H*), 6.92 (t, 2H, Ar-*H*, $^2J_{P-H}$ = 7Hz), 2.85 (m, 2H, C*H*^{i}Pr$_2$), 2.43 (m, 2H C*H*^{i}Pr$_2$), 1.42 (m, 12H, CH(C*H*$_3$)$_2$), 1.05 (m, 12H, CH(C*H*$_3$)$_2$).

^{13}C {^{1}H} NMR (100.62 MHz, benzene-d_6) δ = 156.4 (dt, 2C ipso$^1J_{P-C}$ = 36.3Hz, $^2J_{C-P}$ = 18.6Hz), 133.9 (dt, 2C ipso$^1J_{C-P}$ = 23.3Hz, $^2J_{C-P}$ = 19.5Hz), 132.1 (d, 2C, $^3J_{C-P}$ = 1.4 Hz), 131.4 (d, 2C, $^3J_{C-P}$ = 1.2 Hz), 130.2 (d virtual t, 2C, $^2J_{C-P}$ = 14.3Hz, $^{trans}J_{P-C}$ = 14.1Hz, $^3J_{C-P}$ = 10.2Hz), 126.5 (dt, 2C, J_{C-P} = 3.3Hz, J_{C-P} = 1.7 Hz), 27.9 (t, 1C, C*H*(CH$_3$)$_2$, J_{P-C} = 11 Hz), 26.9 (broad signal 2C), 26.0 (t, 1C, C*H*(CH$_3$)$_2$, J_{C-P} = 12 Hz), 19.6 (d, 2C, CH(C*H*$_3$)$_2$, $^2J_{C-P}$ = 2 Hz), 19.4 (broad s, 2C, CH(C*H*$_3$)$_2$), 18.9 (d, 2C, CH(C*H*$_3$)$_2$, $^2J_{C-P}$ = 2 Hz), 18.8 (broad s, 2C, CH(C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR (121.4 MHz; benzene-d_6) δ = 110.78 (t, 1P, $^3J_{P-P}$ = 8Hz), 58.4 (d, 2P, $^3J_{P-P}$ = 8 Hz).

Anal. Calcd. For $C_{24}H_{36}P_3PdCl$: C, 51.54; H, 6.49%. Found: C, 51.42; H, 6.46%.

Synthesis of (Ph-PPP)PdCl (2): The synthetic procedure was the same followed for complex 1.

(COD)PdCl$_2$ (0.232 g; 0.81 mmol) and the Ph-PPP-H ligand (0.450 g; 0.81 mmol) in THF (10mL) and NEt$_3$ (0.308g, 2.38 mmol). Yield 68% (0.383 g).

^{1}H NMR (300 MHz, benzene-d_6): δ = 8.43 (dd, 2H, Ar-*H*, $^2J_{P-H}$ = 7Hz, $^1J_{H-H}$ = 3Hz), 7.67 (t, 2H, Ar-*H*, J_{H-H} = 8Hz), 7.49 (b, 2H, Ar-*H*), 7.37 (t, 2H, Ar-*H*, $^2J_{P-H}$ = 7Hz), 7.13 (b, 16H, Ar-*H*), 6.78 (t, 2H, Ar-*H*, $^1J_{H-H}$ = 7Hz).

^{13}C{^{1}H} NMR (100.62 MHz, CD$_2$Cl$_2$) δ = 161.1 (t, J_{C-P} = 12 Hz, C), 135.5 (d, J_{C-P} = 18 Hz, CH), 134.9 (d, J_{C-P} = 17 Hz, CH), 134.5 (t, J_{C-P} = 11Hz, CH), 134.1 (t, J_{C-P} = 12 Hz, C), 131.2 (d, J_{C-P} = 15Hz, CH), 129.7 (t, J_{C-P} = 9 Hz, CH), 129.3 (d, J_{C-P} = 14 Hz), 129.1 (t, J_{C-P} = 8 Hz, CH), 128.6 (d, J_{C-P} = 18 Hz). ^{31}P{^{1}H } NMR (161.97 MHz, benzene-d_6) δ = 123.18 (t, 1P, $^3J_{P-P}$ = 24Hz), 62.2(d, 2P, $^3J_{P-P}$ = 24Hz).

Anal. Calcd. for C$_{36}$H$_{28}$ClP$_3$Pd: C, 62,18; H, 4,06%. Found: C, 62.33; H, 4.52%.

Representative procedure for palladium-catalyzed allylation of electrophiles: To a solution of appropriate quantity of the catalyst (0.0175mmol) in DMF (1.9 mL) was added the aldehyde (0.35 mmol) and the allylstannane (0.55 mmol). The resulting solution was then heated at the designated temperature for the allotted time (Table 2). Subsequently, the reaction mixture was quenched by addition of a saturated aqueous solution of sodium bicarbonate and extracted with ethyl acetate. The collected organic phases were washed with a saturated aqueous solution of sodium chloride, dehydrated, concentrated to dryness, and then purified by chromatography with hexane/ethyl acetate as the eluent. For solvent free reactions the reaction mixtures were directly purified by chromatography.

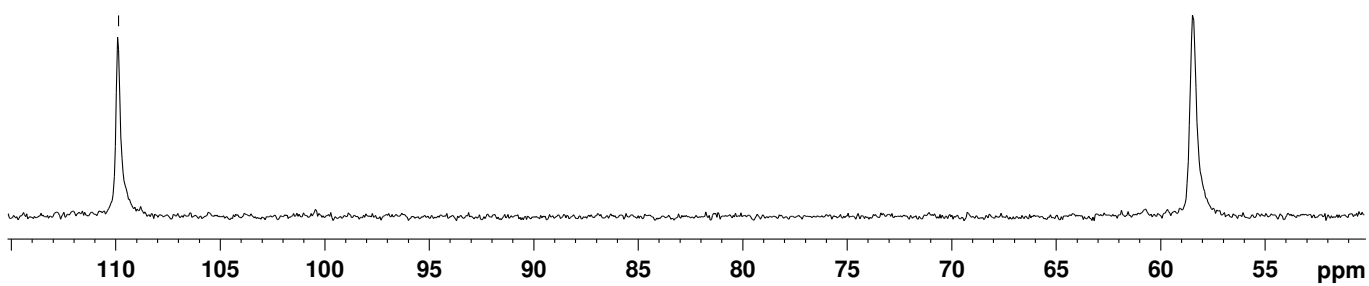**Figure S1:** $^{31}P\{^1H\}$ NMR spectrum of complex **1** in C_6D_6.

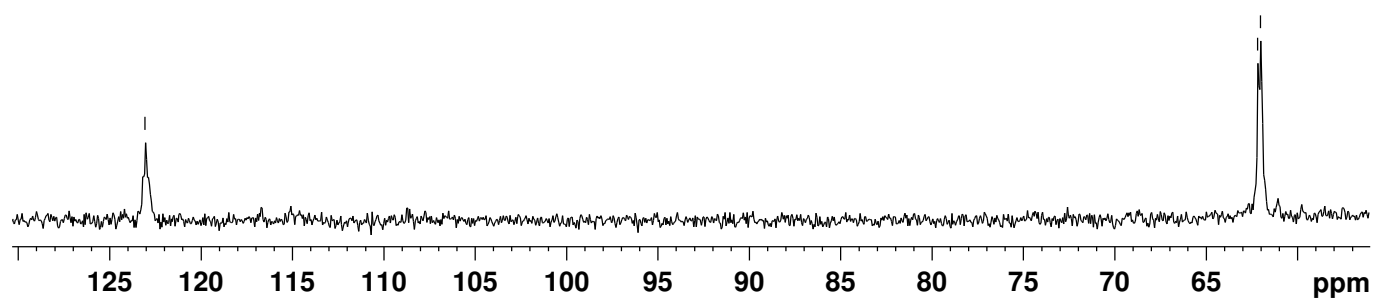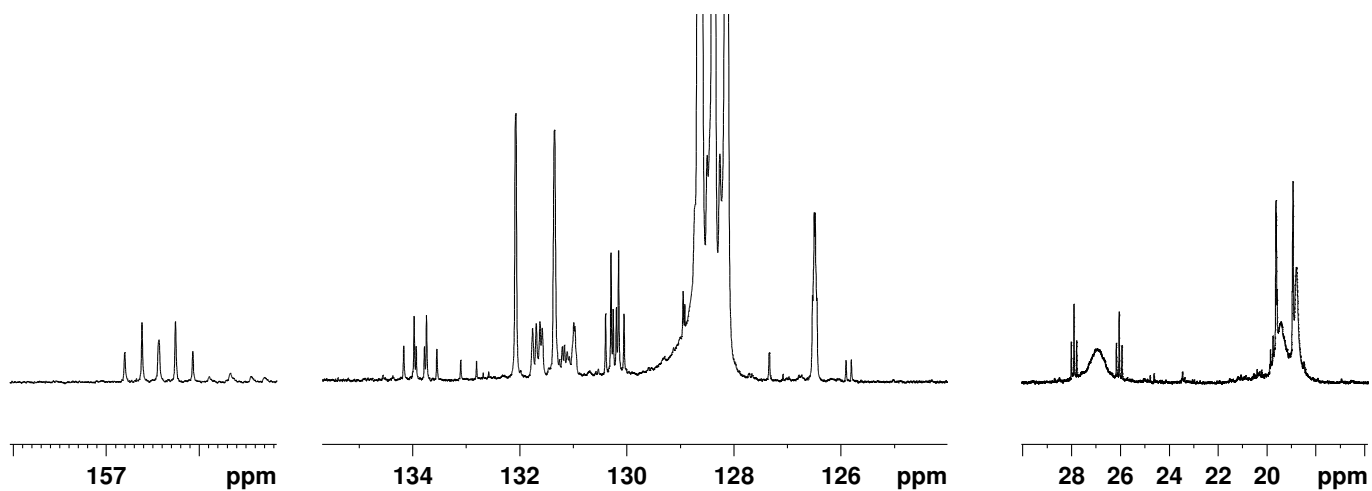**Figure S2:** $^{31}P\{^1H\}$ NMR spectrum of complex **2** in C_6D_6.

Figure S3: Representative regions of $^{13}C\{^1H\}$ NMR spectrum of complex **1** in C_6D_6.

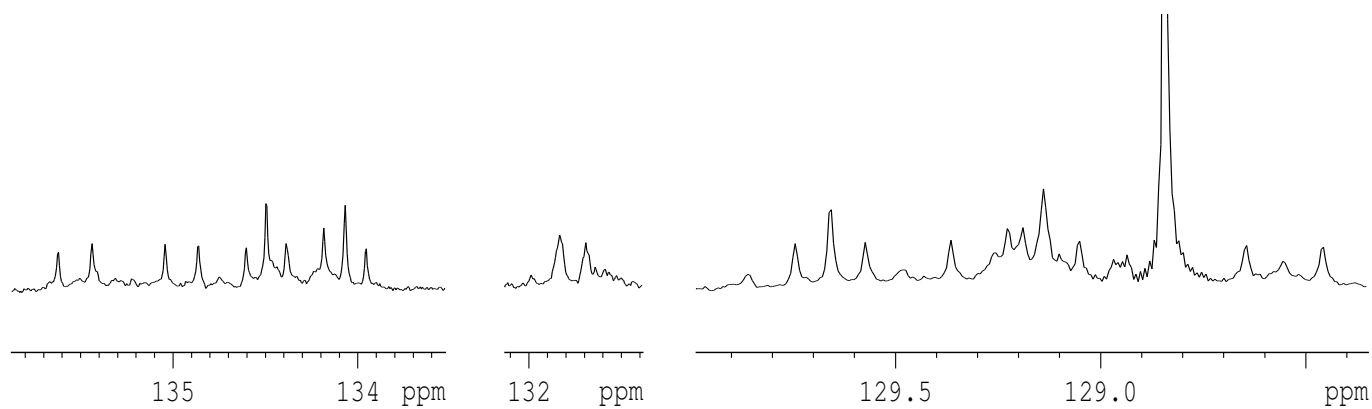**Figure S4:** Representative regions of $^{13}C\{^1H\}$ NMR spectrum of complex **2** in CD_2Cl_2.

II. Experimental details for crystal structure determination

Spatial refinement details.

Refinement of F_2 against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F_2, conventional R-factors (R) are based on F, with F set to zero for negative F_2. The threshold expression of $F_2 > 2 \int (F_2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F_2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles, and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Crystals for X-ray analysis were obtained via vapor diffusion of petroleum ether into a THF solution of the complex **1**. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.
Crystal data for **1**: [C24 H36 Cl P3 Pd], formula weight = 559.29, Monoclinic, P2(1)/n, $a =$ 14.310(4) Å, $b =$ 11.988(5) Å, $c =$ 15.352(7) Å, $\alpha = 90°$, $\beta = 102.12(3)°$, $\gamma = 90°$, $V =$ 2574.7(17) $Å^3$, $Z =$ 4. $Dc =$ 1.359 1.443 Mg/m^3, $F(000) =$ 1152, $T =$ 373 K. An orange crystal mounted in a glass capillary was used for data collection at 100 K on a Smart CCD 1000 diffractometer using graphite monochromatized Mo– Kα radiation.

Table S1. Crystal data and structure refinement for **1**.

Identification code	mm03	
Empirical formula	C24 H36 Cl P3 Pd	
Formula weight	559.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 14.310(4) Å	α = 90°.
	b = 11.988(5) Å	β = 102.12(3)°.
	c = 15.352(7) Å	γ = 90°.
Volume	2574.7(17) Å^3	
Z	4	
Density (calculated)	1.443 Mg/m^3	
Absorption coefficient	1.020 mm^{-1}	
F(000)	1152	
Crystal size	x x mm^3	
Theta range for data collection	1.77 to 40.75°.	

Index ranges	-21<=h<=25, -21<=k<=21, -27<=l<=21
Reflections collected	48836
Independent reflections	14690 [R(int) = 0.1122]
Completeness to theta = 40.75°	87.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14690 / 0 / 270
Goodness-of-fit on F^2	1.209
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.0866
R indices (all data)	R1 = 0.0895, wR2 = 0.0961
Largest diff. peak and hole	3.118 and -1.119 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	5103(1)	8709(1)	2404(1)	13(1)
Cl(1)	6440(1)	9563(1)	3400(1)	24(1)
P(1)	3904(1)	7672(1)	1617(1)	15(1)
P(2)	6045(1)	7786(1)	1604(1)	16(1)
P(3)	3882(1)	9691(1)	2835(1)	16(1)
C(1)	2872(1)	8622(2)	1334(1)	18(1)
C(2)	2091(2)	8480(2)	616(1)	25(1)
C(3)	1274(2)	9119(2)	549(2)	31(1)
C(4)	1200(2)	9907(2)	1205(2)	31(1)
C(5)	1965(2)	10066(2)	1913(1)	26(1)
C(6)	2806(1)	9439(2)	1979(1)	20(1)
C(7)	3654(2)	9264(2)	3926(1)	22(1)
C(8)	3666(2)	7989(2)	3995(2)	31(1)
C(9)	2752(2)	9751(2)	4151(2)	34(1)
C(10)	3980(2)	11222(2)	2879(1)	23(1)
C(11)	4711(2)	11620(2)	3693(2)	34(1)
C(12)	4235(2)	11650(2)	2019(2)	37(1)
C(13)	4280(1)	7200(2)	601(1)	16(1)
C(14)	3675(1)	6670(2)	-114(1)	18(1)
C(15)	4040(1)	6149(2)	-778(1)	19(1)
C(16)	5017(2)	6093(2)	-726(1)	20(1)
C(17)	5634(2)	6573(2)	-10(1)	21(1)
C(18)	5273(1)	7147(2)	645(1)	16(1)
C(19)	6782(1)	6625(2)	2151(1)	22(1)
C(20)	6149(2)	5892(2)	2607(1)	27(1)
C(21)	7657(2)	7032(2)	2824(2)	30(1)
C(22)	6827(1)	8790(2)	1190(1)	22(1)
C(23)	7552(2)	8306(2)	694(2)	31(1)
C(24)	6212(2)	9679(2)	629(2)	28(1)

Table S3. Bond lengths [Å] and angles [°] for **1**.

_____

Pd(1)-P(1)	2.2533(9)
Pd(1)-P(2)	2.2894(8)
Pd(1)-P(3)	2.3146(8)
Pd(1)-Cl(1)	2.4122(10)
P(1)-C(13)	1.842(2)
P(1)-C(1)	1.843(2)
P(2)-C(18)	1.8140(19)
P(2)-C(19)	1.840(2)
P(2)-C(22)	1.845(2)
P(3)-C(6)	1.827(2)
P(3)-C(10)	1.842(2)
P(3)-C(7)	1.846(2)
C(1)-C(2)	1.405(3)
C(1)-C(6)	1.410(3)
C(2)-C(3)	1.384(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.401(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.384(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.405(3)
C(5)-H(5)	0.9500
C(7)-C(9)	1.521(3)
C(7)-C(8)	1.532(3)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.528(3)
C(10)-C(12)	1.530(3)
C(10)-H(10)	1.0000

C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.400(3)
C(13)-C(18)	1.409(3)
C(14)-C(15)	1.388(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.384(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.383(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.403(3)
C(17)-H(17)	0.9500
C(19)-C(21)	1.526(3)
C(19)-C(20)	1.532(3)
C(19)-H(19)	1.0000
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.525(3)
C(22)-C(24)	1.527(3)
C(22)-H(22)	1.0000
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
P(1)-Pd(1)-P(2)	85.06(3)

P(1)-Pd(1)-P(3)	84.17(3)
P(2)-Pd(1)-P(3)	164.429(19)
P(1)-Pd(1)-Cl(1)	170.842(19)
P(2)-Pd(1)-Cl(1)	93.84(3)
P(3)-Pd(1)-Cl(1)	98.55(3)
C(13)-P(1)-C(1)	110.65(9)
C(13)-P(1)-Pd(1)	107.33(7)
C(1)-P(1)-Pd(1)	105.52(7)
C(18)-P(2)-C(19)	104.13(9)
C(18)-P(2)-C(22)	107.83(9)
C(19)-P(2)-C(22)	108.64(10)
C(18)-P(2)-Pd(1)	108.20(7)
C(19)-P(2)-Pd(1)	117.81(7)
C(22)-P(2)-Pd(1)	109.72(7)
C(6)-P(3)-C(10)	103.70(9)
C(6)-P(3)-C(7)	108.86(10)
C(10)-P(3)-C(7)	105.59(10)
C(6)-P(3)-Pd(1)	106.48(7)
C(10)-P(3)-Pd(1)	117.52(7)
C(7)-P(3)-Pd(1)	114.00(7)
C(2)-C(1)-C(6)	118.41(18)
C(2)-C(1)-P(1)	125.13(16)
C(6)-C(1)-P(1)	115.63(14)
C(3)-C(2)-C(1)	120.8(2)
C(3)-C(2)-H(2)	119.6
C(1)-C(2)-H(2)	119.6
C(2)-C(3)-C(4)	120.6(2)
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	119.5(2)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	120.4(2)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	120.23(19)

C(5)-C(6)-P(3)	122.98(17)
C(1)-C(6)-P(3)	116.65(14)
C(9)-C(7)-C(8)	111.44(19)
C(9)-C(7)-P(3)	114.85(15)
C(8)-C(7)-P(3)	109.73(14)
C(9)-C(7)-H(7)	106.8
C(8)-C(7)-H(7)	106.8
P(3)-C(7)-H(7)	106.8
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(12)	110.8(2)
C(11)-C(10)-P(3)	112.03(15)
C(12)-C(10)-P(3)	109.37(15)
C(11)-C(10)-H(10)	108.2
C(12)-C(10)-H(10)	108.2
P(3)-C(10)-H(10)	108.2
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5

H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(18)	117.94(17)
C(14)-C(13)-P(1)	124.07(15)
C(18)-C(13)-P(1)	116.37(13)
C(15)-C(14)-C(13)	120.91(18)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(16)-C(15)-C(14)	120.74(17)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(17)-C(16)-C(15)	119.60(19)
C(17)-C(16)-H(16)	120.2
C(15)-C(16)-H(16)	120.2
C(16)-C(17)-C(18)	120.23(19)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(13)	120.47(17)
C(17)-C(18)-P(2)	122.34(15)
C(13)-C(18)-P(2)	117.12(14)
C(21)-C(19)-C(20)	110.72(18)
C(21)-C(19)-P(2)	112.16(15)
C(20)-C(19)-P(2)	107.74(14)
C(21)-C(19)-H(19)	108.7
C(20)-C(19)-H(19)	108.7
P(2)-C(19)-H(19)	108.7
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5

H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-C(24)	110.88(18)
C(23)-C(22)-P(2)	116.70(16)
C(24)-C(22)-P(2)	109.22(15)
C(23)-C(22)-H(22)	106.5
C(24)-C(22)-H(22)	106.5
P(2)-C(22)-H(22)	106.5
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

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Symmetry transformations used to generate equivalent atoms

Table S4. Anisotropic displacement parameters $(\text{Å}^2 \text{x } 10^3)$ for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 \, a^{*2}U^{11} + ... \; + 2\, h \, k \, a^* \, b^* \, U^{12} \,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	10(1)	16(1)	15(1)	-1(1)	3(1)	0(1)
Cl(1)	14(1)	28(1)	29(1)	-12(1)	-1(1)	0(1)
P(1)	11(1)	18(1)	17(1)	1(1)	3(1)	-1(1)
P(2)	10(1)	18(1)	18(1)	-4(1)	2(1)	0(1)
P(3)	14(1)	18(1)	18(1)	1(1)	7(1)	2(1)
C(1)	11(1)	23(1)	22(1)	6(1)	5(1)	0(1)
C(2)	18(1)	30(1)	25(1)	3(1)	1(1)	0(1)
C(3)	15(1)	39(1)	35(1)	9(1)	-4(1)	2(1)
C(4)	17(1)	34(1)	41(1)	8(1)	4(1)	7(1)
C(5)	16(1)	32(1)	29(1)	3(1)	6(1)	5(1)
C(6)	13(1)	24(1)	24(1)	5(1)	6(1)	1(1)
C(7)	22(1)	26(1)	19(1)	2(1)	9(1)	-1(1)
C(8)	40(1)	30(1)	27(1)	8(1)	16(1)	-1(1)
C(9)	30(1)	47(1)	29(1)	4(1)	17(1)	7(1)
C(10)	23(1)	17(1)	31(1)	2(1)	10(1)	5(1)
C(11)	31(1)	22(1)	49(1)	-10(1)	6(1)	2(1)
C(12)	48(2)	25(1)	44(1)	9(1)	20(1)	-1(1)
C(13)	15(1)	17(1)	16(1)	2(1)	3(1)	-1(1)
C(14)	16(1)	20(1)	17(1)	1(1)	0(1)	-3(1)
C(15)	19(1)	19(1)	17(1)	1(1)	-1(1)	-3(1)
C(16)	22(1)	19(1)	17(1)	-4(1)	4(1)	-2(1)
C(17)	18(1)	22(1)	23(1)	-6(1)	6(1)	-1(1)
C(18)	14(1)	18(1)	17(1)	-3(1)	3(1)	-1(1)
C(19)	17(1)	24(1)	24(1)	-7(1)	-1(1)	6(1)
C(20)	29(1)	23(1)	28(1)	-1(1)	0(1)	6(1)
C(21)	23(1)	29(1)	33(1)	-7(1)	-7(1)	4(1)
C(22)	17(1)	28(1)	23(1)	-9(1)	8(1)	-6(1)
C(23)	22(1)	39(1)	36(1)	-12(1)	16(1)	-7(1)
C(24)	33(1)	26(1)	29(1)	-2(1)	12(1)	-5(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2x 10 ^{3})
for **1**.

	x	y	z	U(eq)
H(2)	2126	7939	172	30
H(3)	757	9022	53	37
H(4)	631	10329	1164	37
H(5)	1920	10603	2358	31
H(7)	4204	9543	4389	26
H(8A)	3619	7768	4599	47
H(8B)	4263	7702	3865	47
H(8C)	3123	7681	3565	47
H(9A)	2190	9444	3745	50
H(9B)	2758	10565	4086	50
H(9C)	2727	9560	4766	50
H(10)	3341	11534	2918	27
H(11A)	5327	11261	3701	51
H(11B)	4490	11424	4236	51
H(11C)	4783	12431	3664	51
H(12A)	4186	12465	1999	56
H(12B)	3792	11331	1505	56
H(12C)	4890	11427	2003	56
H(14)	3005	6667	-145	22
H(15)	3616	5827	-1273	23
H(16)	5261	5727	-1180	24
H(17)	6305	6514	39	25
H(19)	7002	6172	1685	27
H(20A)	6490	5203	2818	41
H(20B)	5557	5710	2180	41
H(20C)	5994	6296	3114	41
H(21A)	7450	7479	3283	45
H(21B)	8056	7489	2518	45
H(21C)	8025	6389	3102	45
H(22)	7203	9182	1726	26

H(23A)	7220	8039	108	46
H(23B)	7890	7684	1037	46
H(23C)	8013	8885	620	46
H(24A)	6624	10265	472	43
H(24B)	5773	10003	972	43
H(24C)	5843	9337	84	43