Supporting Information

Highly Efficient Asymmetric Lewis Acid Catalysis with Platinum Group Complexes of Conformationally Flexible 1,3-Butadiene Bridged Diphosphines, NUPHOS

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General Procedures. All manipulations involving air sensitive materials were carried out in an inert atmosphere glove box or using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Diethyl ether and hexane were distilled from potassium/sodium

alloy, tetrahydrofuran from potassium, dichloromethane from calcium hydride and methanol from magnesium. Cyclopentadiene was collected immediately before use, by distillation during thermal cracking of dicyclopentadiene. BIPHEP was purchased from Strem. Unless otherwise stated, commercially purchased materials were used without further purification. Deuteriochloroform was pre-dried with calcium hydride and vacuum transferred and stored over 4 Å molecular sieves. Acryloyl-*N*-oxazolidinones **6a** and **6b** were prepared according to published methods.¹ The platinum complexes [(NUPHOS)Pt{(*S*)-BINOL}] (**2a-e**)² and the palladium complexes [(1,2,3,4-*R*₄-NUPHOS)PdCl₂] (*R* = Me, Ph)³ and [(cycloocta-1,5-diene)PdCl₂]⁴ were prepared as previously described. ¹H and ³¹P{¹H} and ¹³C{¹H} NMR spectra were recorded on a JEOL LAMBDA 500 or Bruker AC 200, AMX 300 and DRX 500 machines. Optical rotations were measured on a Perkin Elmer 241 spectropolarimeter and are reported as follow: [α]_D (*c* g/100 mL, solvent). Purification of reaction products was carried out by column chromatography on reagent silica gel (60-200 mesh). Analytical high performance liquid chromatography (HPLC) was performed on an Agilent 110 Series HPLC equipped with a variable wavelength detector using a Daicel Chiralcel OD-H column. Enantiomeric excess was calculated from the HPLC profile.⁵

Synthesis of λ-[[1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene]palladium{(*S*)-BINOL}] λ-(3a**).** A solution of dichloro[[1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene]palladium] (0.350 g, 0.53 mmol) in a mixture of dichloromethane (20 mL) and toluene (10 mL) was treated with sodium *tert*-butoxide (0.104 g, 1.08 mmol) and (*S*)-BINOL (0.155 g, 0.54 mmol) at room temperature and stirred for 5 hours. The resulting dark brown solution was filtered through celite and the solvent evaporated. The solid residue, containing a 1:1 mixture of diastereoisomers, was washed with hexane and crystallized by slow diffusion of a chloroform solution layered with hexane at room temperature to give 0.177 g of enantiopure λ-**3a**, corresponding to an overall yield of 38% based on a maximum of 0.53 mmol. In a separate experiment a near 1:1 diastereoisomeric mixture of **3a** was dissolved in chloroform (0.020 g in 0.7 mL) and the extent of diastereointerconversion probed using ³¹P NMR spectroscopy. After 20 h the sample was clearly enriched in the thermodynamically more

stable diastereoisomer which confirms that diastereointerconversion occurs at room temperature. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3 , δ): 25.8 (s, PPh_2). ^1H NMR (500.13 MHz, CDCl_3 , δ): 8.10 (br, 4H, aromatic), 7.94 (br quart, $J = 6.5$ Hz, 6H, aromatic), 7.65 (d, $J = 8.2$ Hz, 2H, aromatic), 7.50-7.44 (m, 4H, aromatic), 7.42 (t, $J = 8.7$ Hz, 4H, aromatic), 7.32 (t, $J = 7.3$ Hz, 2H, aromatic), 7.23 (t, $J = 7.8$ Hz, 4H, aromatic), 6.95 (br d, $J = 2.0$ Hz, 2H, aromatic), 6.27 (d, $J = 8.7$ Hz, 2H, aromatic), 1.44 (t, $J = 5.6$ Hz, 6H, CH_3), 1.15 (s, 6H, CH_3). Anal. Calcd for $\text{C}_{52}\text{H}_{44}\text{O}_2\text{P}_2\text{Pd}$: C, 71.85; H, 5.10. Found: C, 71.72; H, 5.01. $[\alpha]_{\text{D}} = +8.69$ (c 1.0, CHCl_3).

Synthesis of δ -[1,4-bis(diphenylphosphino)-1,2,3,4-tetraphenyl-1,3-butadiene]palladium{(S)-BINOL}] δ -(3c). Compound δ -3c was prepared according to the procedure described above for λ -3a and isolated as a dark brown solid in 54% yield by slow diffusion of a dichloromethane solution layered with hexane at room temperature. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3 , δ): 20.7 (s, PPh_2). ^1H NMR (500.13 MHz, CDCl_3 , δ): 9.03 (br, 4H, aromatic), 7.95 (br, 6H, aromatic), 7.6 (d, $J = 8.1$ Hz, 2H, aromatic), 7.42 (d, $J = 8.7$ Hz, 2H, aromatic), 6.92 (t, $J = 6.6$ Hz, 2H, aromatic), 6.90-6.57 (m, 26H, aromatic), 6.52 (t, $J = 7.2$ Hz, 4H, aromatic), 6.76 (br d, $J = 7.9$ Hz, 2H, aromatic), 6.70 (d, $J = 7.2$ Hz, 2H, aromatic). Anal. Calcd for $\text{C}_{72}\text{H}_{52}\text{O}_2\text{P}_2\text{Pd}$: C, 77.38; H, 4.69. Found: C, 77.57; H, 4.88. $[\alpha]_{\text{D}} = -21.56$ (c 1.0, CHCl_3).

λ -[1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene] PtCl_2] λ -(8a). A solution of enantiopure λ -[1,4-bis(diphenylphosphino)-1,2,3,4-tetramethyl-1,3-butadiene]platinum{(S)-BINOL}] (2a) (1.1 g, 1.15 mmol) in dichloromethane (20 mL) was treated with a diethylether solution of HCl (2.5 mL, 2.5 mmol, 1.0 M solution in diethylether). Addition of HCl resulted in an immediate color change from deep yellow to near colorless. After 10 mins the solution was filtered, the solvent removed under vacuum and the resulting residue washed with diethylether (5 x 10 mL) and hexane (5 x 10 mL). Crystallization of the product by slow diffusion of a dichloromethane solution layered with hexane at room temperature gave pale yellow λ -8a in 71% yield (0.607 g). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5

MHz, CDCl₃, δ): 6.7 (t, $J_{\text{PtP}} = 3660$ Hz, PPh₂). ¹H NMR (300.0 MHz, CDCl₃, δ): 8.36 (br, 4H, C₆H₅), 7.58 (m, 8H, C₆H₅), 7.27 (m, 8H, C₆H₅), 1.23 (d, $J_{\text{PH}} = 11.2$ Hz, 6H, CH₃), 1.18 (s, 6H, CH₃). Anal. Calcd for C₃₂H₃₂Cl₂P₂Pt: C, 51.62; H, 4.33. Found: C, 52.06; H, 4.67. $[\alpha]_{\text{D}} = +0.216$ (c 1.0, CHCl₃).

δ -[1,4-bis(diphenylphosphino)-1,2,3,4-tetraphenyl-1,3-butadiene]PtCl₂ δ -(8c). Compound **δ -8c** was isolated as an off-white solid in 63% yield (0.594 g) according to the procedure described above for **λ -8a**. ³¹P{¹H} NMR (121.5 MHz, CDCl₃, δ): 1.9 (t, $J_{\text{PtP}} = 3607$ Hz, PPh₂). ¹H NMR (500.13 MHz, CDCl₃, 232 K, δ): 9.57 (br m, 4H, C₆H₅), 7.9 (br m, 6H, C₆H₅), 7.2 (m, 6H, C₆H₅), 6.88, (m, 4H, C₆H₅), 6.7 (t, $J = 7.3$ Hz, 2H, C₆H₅), 6.65 (m, 6H, C₆H₅), 6.54 (t, $J = 7.9$ Hz, 4H, C₆H₅), 6.18 (br, 4H, C₆H₅), 6.11 (d, $J = 7.3$ Hz, 4H, C₆H₅). Anal. Calcd for C₅₂H₄₀Cl₂P₂Pt: C, 62.91; H, 4.06. Found: C, 63.23; H, 4.44. $[\alpha]_{\text{D}} = -9.07$ (c 1.0, CHCl₃).

Synthesis of [(2R,3R,4aR,8aR)-6,7-Bis-[1-diphenylphosphanyl-1-phenylmeth-(Z)-ylidene]-2,3-dimethoxy-2,3-dimethyloctahydro-1,4-benzodioxin]PdCl₂ (10). A solution of [(cycloocta-1,5-diene)PdCl₂] (0.250 g, 0.88 mmol) in dichloromethane (8-10 mL) was treated with a dichloromethane solution (7-10 mL) of diphosphine **9** (0.809 g, 0.88 mmol) and stirred vigorously for *ca.* 2 hrs. The reaction mixture was filtered and the solvent removed to leave a yellow-orange solid residue. Crystallization by slow diffusion of n-hexane into a dichloromethane solution at room temperature gave **10** as a microcrystalline yellow solid in 71 % yield (0.68 g). ³¹P{¹H} NMR (121.4 MHz, CDCl₃, δ) 21.5 (s, PPh₂). ¹H NMR (500.1 MHz, CDCl₃, δ): 8.8 (m, 4H, C₆H₅), 7.8-6.7 (m, 6.9 Hz, 16H C₆H₅), 5.61 (t, $J = 6.9$ Hz, 2H, C₆H₅), 6.19 (br s, 2H, C₆H₅), 6.16 (d, $J = 7.1$ Hz, 2H, C₆H₅), 5.86 (d, $J = 7.5$ Hz, 2H, C₆H₅), 5.52 (br s, 2H, C₆H₅), 3.24 (m, 2H, CH), 2.94, (s, 6H, OMe), 2.01 (dd, $J = 10.2, 2.9$ Hz, 2H, CH_aH_b), 1.6 (m, 2H, CH_aH_b), 1.13 (s, 6H, CH₃). Anal. Calcd for C₅₀H₄₈O₄P₂PdCl₂: C, 63.07; H, 5.08. Found: C, 63.32; H, 5.27 %.

General procedure for platinum-catalyzed enantioselective Diels-Alder reaction between cyclopentadiene and acryloyl-N-oxazolidinone 6a with catalyst precursors 2a-e. A solution of **2a**

(0.0153 g, 0.016 mmol) and dieneophile **6a** (0.0225 g, 0.16 mmol) in dichloromethane (3 mL) was treated with trifluoromethanesulfonic acid (2.2 μ L, 0.023 mmol), which resulted in an immediate color change from deep yellow to near colorless. After stirring for 15 min the solution was cooled to -78 °C and freshly distilled cyclopentadiene (0.1 mL, 1.48 mmol) added. The reaction mixture was warmed to -60 °C and stirred overnight after which time the resulting solution was quenched with (*S,S*)-dpda and a ^{31}P NMR spectrum recorded to determine the extent of atropinversion. The crude product was purified by column chromatography over silica gel (60-200 mesh, 30% ethyl acetate/hexane). The *endo/exo* ratio was obtained from ^1H NMR spectroscopy and the enantiomeric excess was calculated from the HPLC profile (1 mL/min flow rate, hexane:2-propanol = 90:10). The retention times of the *endo* and *exo* isomers were 16.93 min (*exo*₁), 17.71 min (*exo*₂), 18.47 min (*endo*_{2S}), 20.41 min (*endo*_{2R}). The absolute configuration of the *endo* cycloadduct was assigned by comparison with the retention times of samples prepared from (*R*)- and [(*S*)-BINAP]PtCl₂].

General procedure for palladium-catalyzed enantioselective Diels-Alder reaction between cyclopentadiene and acryloyl-*N*-oxazolidinone **6a with catalyst precursors λ -**3a** and δ -**3c**.** A solution of λ -**3a** (0.0153 g, 0.016 mmol) and dieneophile **6a** (0.0225 g, 0.16 mmol) in dichloromethane (3 mL) was cooled to -40 °C and treated with trifluoromethanesulfonic acid (2.2 μ L, 0.023 mmol). After stirring for 15 min the solution was cooled to -78 °C and freshly distilled cyclopentadiene (0.1 mL, 1.48 mmol) added. The reaction mixture was warmed to -60 °C and stirred overnight after which time the resulting solution was quenched with (*S,S*)-dpda. The crude product was purified by column chromatography over silica gel (60-200 mesh, 30% ethyl acetate/hexane) and the *endo:exo* ratio and *endo* enantioselectivity determined.

General procedure for enantioselective Diels-Alder reaction between cyclopentadiene and acryloyl-*N*-oxazolidinone **6a with platinum dichloride catalyst precursors λ -**8a** and δ -**8c**.** A solution of λ -[(1,2,3,4-Me₄-NUPHOS)PtCl₂] (0.025 g, 0.037 mmol) and dienophile **6a** was treated with silver perchlorate (0.0082 g, 0.067 mmol) and stirred for 30 mins. The resulting catalyst solution

was cooled to -78 °C and freshly distilled cyclopentadiene added (0.1 mL, 1.48 mmol). After stirring at -60 °C for 20 h the reaction mixture was quenched with (*S,S*)-dpeda and the crude product purified by column chromatography.

General procedure for enantioselective Diels-Alder reaction between cyclopentadiene and acryloyl-*N*-oxazolidinone **6b with platinum dichloride catalyst precursors **λ-8a** and **δ-8c**.** Catalyst mixtures were prepared as described above for dienophile **6a**. After addition of cyclopentadiene the reaction mixture was warmed to -20 °C and stirred for 40 h after which time (*S,S*)-dpeda was added to quench the reaction. The ³¹P NMR spectrum of the crude reaction mixture contained two signals corresponding to the diastereoisomeric amine complexes λ/δ-[(NUPHOS)Pt{(*S,S*)-dpeda}] in a 97:3 ratio confirming that atropinversion during reaction was slow. The crude residue was purified by column chromatography over silica gel (60-200 mesh, 30% ethyl acetate/hexane). The *endo/exo* ratio was determined by ¹H NMR spectroscopy and the *endo* enantioselectivity by chiral HPLC analysis (1.0 mL/min flow rate, 94% hexane, 4% ethyl acetate, 2% 2-propanol). Retention times of the *endo* and *exo* isomers were 16.8 min (*exo*₁ and *exo*₂), 19.02 min (*endo*_{2S}), 21.78 min (*endo*_{2R}).

Crystal structure determination of compound **3a.** Crystals of **3a** suitable for single-crystal X-ray crystallography were grown from a dichloromethane solution layer with hexane at room temperature. Data was collected on a Bruker SMART CCD diffractometer using SAINT-NT software⁶ with Mo K α radiation (λ = 0.71073 Å) at low temperature. Details of crystal data and other information are presented in Table 1. The structure was solved using direct methods and refined with the SHELXTL program package⁷ and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealized positions and a riding model was used for subsequent refinement.

References

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Figure 1 Molecular Structure of λ -[{1,2,3,4,-Me₄-NUPHOS}Pd(*S*)-BINOL}] (**3a**)

Table 1 Crystal data and structure refinement for compound **3a.3CH₂Cl₂**

Identification code	sd045m	
Empirical formula	C ₅₂ H ₄₄ O ₂ P ₂ Pd.3CH ₂ Cl ₂	
Formula weight	1123.99	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>P</i> 2(1)2(1)2(1)	
Unit cell dimensions	a = 14.8284(9) Å	α = 90°.
	b = 15.9787(9) Å	β = 90°.
	c = 21.4250(13) Å	γ = 90°.
Volume	5076.4(5) Å ³	
Z	4	
Density (calculated)	1.471 g cm ⁻³	
Absorption coefficient	0.786 mm ⁻¹	
F(000)	2296	
Crystal size	0.30 x 0.22 x 0.16 mm ³	
Theta range for data collection	1.59 to 23.40°.	
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 17, -23 ≤ l ≤ 23	
Reflections collected	24878	
Independent reflections	7263 [R(int) = 0.3394]	
Completeness to theta = 23.40°	98.9 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7263 / 0 / 599	
Final R indices [I > 2σ(I)] ^a	R1 = 0.1117, wR2 = 0.2350	
R indices (all data) ^b	R1 = 0.1666, wR2 = 0.2817	
GOF ^c (S) ^c	1.054	
Absolute structure parameter	-0.12(8)	
Largest diff. peak and hole	1.865 and -1.777 e.Å ⁻³	

a) Conventional $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ for “observed” reflections having $F_o^2 > 2\sigma(F_o^2)$.

b) $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ for all data

c) $GOF = [\sum w(F_o^2 - F_c^2)^2 / (\text{no. unique reflns} - \text{no. of params})]^{1/2}$

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

	x	y	z	$U(\text{eq})$
Pd(1)	-5768(1)	-2640(1)	4608(1)	26(1)
P(1)	-5561(2)	-1555(3)	3950(2)	27(1)
C(11A)	-4524(9)	-1665(11)	3522(7)	27(4)
C(12A)	-4302(10)	-1071(11)	3082(8)	36(4)
C(13A)	-3535(10)	-1163(15)	2682(8)	47(5)
C(14A)	-3011(9)	-1861(15)	2755(9)	47(5)
C(15A)	-3194(9)	-2447(15)	3196(9)	51(6)
C(16A)	-3972(8)	-2358(14)	3588(7)	37(4)
C(11B)	-6464(9)	-1600(10)	3373(8)	29(4)
C(12B)	-6316(10)	-1677(12)	2752(8)	37(4)
C(13B)	-7049(9)	-1730(11)	2327(8)	31(4)
C(14B)	-7927(10)	-1678(12)	2578(8)	37(4)
C(15B)	-8070(10)	-1623(13)	3208(9)	41(5)
C(16B)	-7334(9)	-1601(11)	3620(8)	29(4)
C(2)	-5560(9)	-453(11)	4213(7)	29(4)
C(21)	-6327(9)	92(11)	4005(8)	34(4)
C(3)	-4911(9)	-153(11)	4604(8)	32(4)
C(31)	-4857(12)	722(11)	4789(8)	37(4)
C(4)	-4167(10)	-705(10)	4816(6)	26(3)
C(41)	-3253(9)	-441(13)	4577(10)	45(5)
C(5)	-4281(9)	-1349(11)	5184(7)	28(4)
C(51)	-3543(9)	-2006(11)	5356(9)	40(4)
P(6)	-5411(2)	-1779(3)	5393(2)	24(1)
C(61A)	-6208(10)	-971(10)	5578(7)	26(4)
C(62A)	-7124(10)	-1159(12)	5477(8)	34(4)
C(63A)	-7795(10)	-626(13)	5714(9)	43(5)
C(64A)	-7565(10)	98(14)	6021(9)	44(5)
C(65A)	-6638(14)	311(15)	6110(9)	55(5)
C(66A)	-6001(10)	-243(12)	5882(8)	35(4)
C(61B)	-5269(8)	-2207(10)	6182(7)	26(4)
C(62B)	-4716(9)	-1762(12)	6610(8)	34(4)
C(63B)	-4688(10)	-2026(13)	7230(8)	38(5)
C(64B)	-5186(9)	-2712(12)	7426(8)	34(4)

C(65B)	-5725(11)	-3160(10)	6994(7)	31(4)
C(66B)	-5760(10)	-2868(9)	6380(7)	28(4)
O(1A)	-6067(6)	-3658(7)	5119(5)	27(3)
C(1A)	-5529(9)	-4320(11)	5023(8)	33(4)
C(2A)	-4812(9)	-4460(13)	5469(8)	40(5)
C(3A)	-4245(9)	-5125(9)	5420(7)	27(3)
C(4A)	-4344(9)	-5712(10)	4939(8)	29(4)
C(5A)	-3781(10)	-6422(12)	4871(9)	41(5)
C(6A)	-3891(10)	-6979(12)	4407(9)	36(4)
C(7A)	-4552(10)	-6823(13)	3931(8)	39(5)
C(8A)	-5083(10)	-6146(12)	3975(8)	34(4)
C(9A)	-5031(9)	-5556(11)	4468(6)	27(4)
C(10A)	-5640(8)	-4883(9)	4535(7)	21(3)
O(1B)	-5815(7)	-3390(7)	3826(5)	30(2)
C(1B)	-6429(10)	-4000(12)	3783(7)	30(4)
C(2B)	-7143(9)	-3882(12)	3306(7)	30(4)
C(3B)	-7785(9)	-4473(12)	3236(8)	34(4)
C(4B)	-7805(9)	-5203(12)	3586(8)	33(4)
C(5B)	-8499(10)	-5839(13)	3522(9)	40(5)
C(6B)	-8491(11)	-6514(13)	3872(9)	43(5)
C(7B)	-7800(12)	-6682(14)	4314(9)	48(5)
C(8B)	-7125(10)	-6085(11)	4382(8)	31(4)
C(9B)	-7092(9)	-5358(11)	4047(7)	26(4)
C(10B)	-6396(10)	-4728(12)	4094(7)	29(4)
C(1S)	-4870(12)	-3579(12)	2517(8)	39(4)
Cl(1S)	-5693(3)	-3841(3)	1945(2)	50(1)
Cl(2S)	-4258(4)	-4484(3)	2753(3)	60(1)
C(2S)	-1579(12)	-4366(14)	12450(10)	54(6)
Cl(3S)	-1868(4)	-3656(4)	11837(3)	62(2)
Cl(4S)	-571(3)	-4904(4)	12271(3)	58(1)
C(3S)	-4005(13)	-1279(18)	8943(9)	67(7)
Cl(5S)	-3975(6)	-2330(6)	9153(4)	112(3)
Cl(6S)	-3102(5)	-992(8)	8479(4)	140(5)

Table 3 Bond lengths [$\text{\AA}$] and angles [$^\circ$] for compound **3a**.

Pd(1)-O(1A)	2.010(11)
Pd(1)-O(1B)	2.061(11)
Pd(1)-P(6)	2.235(4)
Pd(1)-P(1)	2.256(5)
P(1)-C(11A)	1.799(14)
P(1)-C(11B)	1.823(15)
P(1)-C(2)	1.848(18)
C(11A)-C(12A)	1.38(2)
C(11A)-C(16A)	1.38(2)
C(12A)-C(13A)	1.43(2)
C(13A)-C(14A)	1.37(3)
C(14A)-C(15A)	1.36(3)
C(15A)-C(16A)	1.43(2)
C(11B)-C(12B)	1.35(2)
C(11B)-C(16B)	1.40(2)
C(12B)-C(13B)	1.42(2)
C(13B)-C(14B)	1.41(2)
C(14B)-C(15B)	1.37(3)
C(15B)-C(16B)	1.40(2)
C(2)-C(3)	1.36(2)
C(2)-C(21)	1.50(2)
C(3)-C(31)	1.45(3)
C(3)-C(4)	1.48(2)
C(4)-C(5)	1.31(2)
C(4)-C(41)	1.51(2)
C(5)-C(51)	1.56(2)
C(5)-P(6)	1.866(15)
P(6)-C(61A)	1.795(16)
P(6)-C(61B)	1.837(16)
C(61A)-C(66A)	1.37(2)
C(61A)-C(62A)	1.41(2)
C(62A)-C(63A)	1.40(2)
C(63A)-C(64A)	1.37(3)
C(64A)-C(65A)	1.43(3)
C(65A)-C(66A)	1.38(3)
C(61B)-C(66B)	1.35(2)

C(61B)-C(62B)	1.42(2)
C(62B)-C(63B)	1.39(2)
C(63B)-C(64B)	1.39(3)
C(64B)-C(65B)	1.42(2)
C(65B)-C(66B)	1.40(2)
O(1A)-C(1A)	1.341(19)
C(1A)-C(10A)	1.39(2)
C(1A)-C(2A)	1.45(2)
C(2A)-C(3A)	1.36(2)
C(3A)-C(4A)	1.40(2)
C(4A)-C(5A)	1.42(2)
C(4A)-C(9A)	1.45(2)
C(5A)-C(6A)	1.34(3)
C(6A)-C(7A)	1.44(2)
C(7A)-C(8A)	1.34(3)
C(8A)-C(9A)	1.42(2)
C(9A)-C(10A)	1.41(2)
C(10A)-C(10B)	1.49(2)
O(1B)-C(1B)	1.34(2)
C(1B)-C(10B)	1.34(2)
C(1B)-C(2B)	1.48(2)
C(2B)-C(3B)	1.35(2)
C(3B)-C(4B)	1.39(2)
C(4B)-C(5B)	1.45(2)
C(4B)-C(9B)	1.47(2)
C(5B)-C(6B)	1.31(3)
C(6B)-C(7B)	1.42(3)
C(7B)-C(8B)	1.39(2)
C(8B)-C(9B)	1.37(2)
C(9B)-C(10B)	1.45(2)
C(1S)-Cl(1S)	1.779(18)
C(1S)-Cl(2S)	1.780(19)
C(2S)-Cl(4S)	1.766(18)
C(2S)-Cl(3S)	1.79(2)
C(3S)-Cl(6S)	1.73(2)
C(3S)-Cl(5S)	1.74(3)
O(1A)-Pd(1)-O(1B)	88.0(4)

O(1A)-Pd(1)-P(6)	98.1(3)
O(1B)-Pd(1)-P(6)	167.7(3)
O(1A)-Pd(1)-P(1)	172.9(3)
O(1B)-Pd(1)-P(1)	86.7(3)
P(6)-Pd(1)-P(1)	88.03(16)
C(11A)-P(1)-C(11B)	106.2(7)
C(11A)-P(1)-C(2)	104.3(7)
C(11B)-P(1)-C(2)	104.2(7)
C(11A)-P(1)-Pd(1)	111.0(6)
C(11B)-P(1)-Pd(1)	107.1(5)
C(2)-P(1)-Pd(1)	122.8(5)
C(12A)-C(11A)-C(16A)	118.6(14)
C(12A)-C(11A)-P(1)	119.0(12)
C(16A)-C(11A)-P(1)	122.2(13)
C(11A)-C(12A)-C(13A)	121.9(17)
C(14A)-C(13A)-C(12A)	117.8(18)
C(15A)-C(14A)-C(13A)	122.0(16)
C(14A)-C(15A)-C(16A)	119.9(18)
C(11A)-C(16A)-C(15A)	119.7(18)
C(12B)-C(11B)-C(16B)	121.5(14)
C(12B)-C(11B)-P(1)	123.4(11)
C(16B)-C(11B)-P(1)	115.0(13)
C(11B)-C(12B)-C(13B)	120.8(14)
C(14B)-C(13B)-C(12B)	117.3(15)
C(15B)-C(14B)-C(13B)	121.4(14)
C(14B)-C(15B)-C(16B)	120.1(14)
C(11B)-C(16B)-C(15B)	118.7(15)
C(3)-C(2)-C(21)	120.8(16)
C(3)-C(2)-P(1)	121.6(12)
C(21)-C(2)-P(1)	117.5(11)
C(2)-C(3)-C(31)	123.1(15)
C(2)-C(3)-C(4)	120.2(15)
C(31)-C(3)-C(4)	116.5(13)
C(5)-C(4)-C(3)	123.8(14)
C(5)-C(4)-C(41)	122.7(14)
C(3)-C(4)-C(41)	113.5(14)
C(4)-C(5)-C(51)	125.6(13)
C(4)-C(5)-P(6)	123.4(11)

C(51)-C(5)-P(6)	109.0(11)
C(61A)-P(6)-C(61B)	98.0(7)
C(61A)-P(6)-C(5)	112.3(7)
C(61B)-P(6)-C(5)	104.8(6)
C(61A)-P(6)-Pd(1)	116.9(5)
C(61B)-P(6)-Pd(1)	119.4(6)
C(5)-P(6)-Pd(1)	105.0(5)
C(66A)-C(61A)-C(62A)	118.0(15)
C(66A)-C(61A)-P(6)	124.7(11)
C(62A)-C(61A)-P(6)	116.6(13)
C(63A)-C(62A)-C(61A)	120.0(17)
C(64A)-C(63A)-C(62A)	120.5(15)
C(63A)-C(64A)-C(65A)	120.2(17)
C(66A)-C(65A)-C(64A)	117(2)
C(61A)-C(66A)-C(65A)	124.0(16)
C(66B)-C(61B)-C(62B)	120.0(15)
C(66B)-C(61B)-P(6)	121.2(12)
C(62B)-C(61B)-P(6)	118.3(12)
C(63B)-C(62B)-C(61B)	118.7(16)
C(64B)-C(63B)-C(62B)	120.8(15)
C(63B)-C(64B)-C(65B)	120.0(15)
C(66B)-C(65B)-C(64B)	117.9(15)
C(61B)-C(66B)-C(65B)	122.5(14)
C(1A)-O(1A)-Pd(1)	115.1(8)
O(1A)-C(1A)-C(10A)	123.7(13)
O(1A)-C(1A)-C(2A)	117.3(16)
C(10A)-C(1A)-C(2A)	118.9(15)
C(3A)-C(2A)-C(1A)	121.7(17)
C(2A)-C(3A)-C(4A)	121.0(14)
C(3A)-C(4A)-C(5A)	123.3(14)
C(3A)-C(4A)-C(9A)	118.0(14)
C(5A)-C(4A)-C(9A)	118.6(16)
C(6A)-C(5A)-C(4A)	122.3(16)
C(5A)-C(6A)-C(7A)	119.6(17)
C(8A)-C(7A)-C(6A)	119.4(17)
C(7A)-C(8A)-C(9A)	123.8(15)
C(10A)-C(9A)-C(8A)	123.2(13)
C(10A)-C(9A)-C(4A)	120.5(14)

C(8A)-C(9A)-C(4A)	116.2(15)
C(1A)-C(10A)-C(9A)	119.6(13)
C(1A)-C(10A)-C(10B)	117.4(13)
C(9A)-C(10A)-C(10B)	123.0(13)
C(1B)-O(1B)-Pd(1)	120.2(9)
O(1B)-C(1B)-C(10B)	124.9(14)
O(1B)-C(1B)-C(2B)	116.1(15)
C(10B)-C(1B)-C(2B)	118.7(16)
C(3B)-C(2B)-C(1B)	119.4(17)
C(2B)-C(3B)-C(4B)	122.9(15)
C(3B)-C(4B)-C(5B)	123.5(15)
C(3B)-C(4B)-C(9B)	119.4(15)
C(5B)-C(4B)-C(9B)	117.1(16)
C(6B)-C(5B)-C(4B)	120.9(16)
C(5B)-C(6B)-C(7B)	122.8(18)
C(8B)-C(7B)-C(6B)	117(2)
C(9B)-C(8B)-C(7B)	123.7(16)
C(8B)-C(9B)-C(10B)	125.5(14)
C(8B)-C(9B)-C(4B)	118.1(14)
C(10B)-C(9B)-C(4B)	116.4(15)
C(1B)-C(10B)-C(9B)	122.8(14)
C(1B)-C(10B)-C(10A)	119.2(14)
C(9B)-C(10B)-C(10A)	117.8(15)
Cl(1S)-C(1S)-Cl(2S)	110.7(10)
Cl(4S)-C(2S)-Cl(3S)	110.6(11)
Cl(6S)-C(3S)-Cl(5S)	112.6(13)

Symmetry transformations used to generate equivalent atoms:

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

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Pd(1)	9(1)	37(1)	30(1)	0(1)	-1(1)	0(1)
P(1)	14(2)	40(3)	27(2)	-1(2)	2(2)	-1(2)
C(11A)	13(7)	44(11)	23(8)	-7(8)	-5(6)	-3(7)
C(12A)	9(7)	49(11)	50(10)	-10(9)	5(7)	-7(7)
C(13A)	14(8)	97(17)	30(10)	-5(10)	15(7)	-9(9)
C(14A)	4(8)	91(17)	45(11)	5(12)	2(6)	-13(9)
C(15A)	12(7)	70(16)	71(13)	-3(13)	-12(7)	10(9)
C(16A)	6(6)	73(14)	31(9)	-6(10)	-1(5)	5(8)
C(11B)	15(7)	30(10)	43(11)	3(8)	0(6)	1(7)
C(12B)	16(8)	61(13)	35(10)	16(9)	1(7)	-1(7)
C(13B)	15(7)	43(11)	36(10)	-7(9)	1(6)	-3(7)
C(14B)	13(8)	55(13)	44(11)	-2(9)	-6(7)	-9(7)
C(15B)	8(7)	64(14)	52(12)	-5(10)	5(7)	1(7)
C(16B)	8(7)	46(11)	33(9)	6(8)	-3(6)	2(7)
C(2)	10(7)	48(11)	28(9)	-16(8)	3(6)	8(7)
C(21)	12(7)	44(12)	46(11)	-3(9)	-3(7)	3(7)
C(3)	25(7)	57(12)	14(7)	-10(9)	0(7)	6(7)
C(31)	46(10)	39(12)	26(10)	1(8)	-2(7)	-10(8)
C(4)	26(7)	34(10)	17(8)	-5(7)	0(6)	0(7)
C(41)	9(7)	65(13)	60(12)	19(12)	3(8)	-1(7)
C(5)	7(6)	49(11)	29(8)	-5(8)	-6(6)	12(7)
C(51)	15(7)	58(12)	47(10)	17(10)	4(7)	8(7)
P(6)	10(2)	30(2)	32(2)	1(2)	-1(2)	0(1)
C(61A)	21(7)	26(10)	31(9)	15(7)	7(6)	-6(7)
C(62A)	26(8)	43(11)	34(10)	12(9)	-6(7)	5(7)
C(63A)	5(7)	64(14)	61(12)	12(11)	-2(7)	5(8)
C(64A)	18(8)	62(15)	52(12)	28(11)	-1(7)	17(8)
C(65A)	68(13)	59(15)	38(11)	-8(11)	-1(9)	11(11)
C(66A)	28(9)	39(12)	37(10)	12(9)	-2(7)	17(7)
C(61B)	9(6)	29(10)	41(9)	12(8)	4(6)	1(6)
C(62B)	6(7)	48(12)	47(11)	-12(9)	-5(6)	-5(7)
C(63B)	17(7)	70(14)	27(10)	-18(9)	-7(6)	10(8)
C(64B)	17(7)	55(12)	30(9)	-4(9)	9(6)	-1(8)

C(65B)	32(8)	20(9)	40(10)	-4(7)	2(8)	2(8)
C(66B)	14(6)	23(9)	46(10)	-28(8)	-1(7)	3(7)
O(1A)	21(5)	21(6)	38(6)	-10(5)	-3(4)	14(4)
C(1A)	11(7)	48(12)	40(10)	32(9)	11(6)	-7(7)
C(2A)	15(7)	76(14)	30(10)	-6(10)	-5(7)	-7(8)
C(3A)	19(6)	34(9)	29(8)	15(8)	4(7)	-4(7)
C(4A)	9(7)	33(10)	44(10)	12(8)	-1(6)	-2(7)
C(5A)	14(7)	47(12)	61(12)	11(11)	4(7)	4(8)
C(6A)	25(8)	31(10)	52(12)	4(9)	7(7)	5(7)
C(7A)	29(8)	53(13)	35(10)	-12(9)	-1(7)	-3(8)
C(8A)	15(7)	52(12)	36(10)	10(9)	0(6)	0(7)
C(9A)	18(7)	52(12)	12(9)	14(7)	0(5)	-19(7)
C(10A)	15(6)	28(9)	22(8)	-3(7)	4(6)	2(6)
O(1B)	21(5)	33(6)	37(6)	5(5)	3(5)	-12(5)
C(1B)	19(8)	46(12)	26(9)	-8(8)	5(6)	7(7)
C(2B)	20(8)	47(11)	24(9)	-5(8)	1(6)	6(7)
C(3B)	9(7)	57(13)	37(10)	-2(9)	1(6)	10(7)
C(4B)	11(7)	55(12)	33(9)	3(9)	3(6)	0(7)
C(5B)	13(7)	55(13)	51(11)	-10(11)	-7(7)	-12(8)
C(6B)	28(9)	56(14)	46(11)	-16(11)	2(8)	-1(9)
C(7B)	45(11)	55(14)	44(11)	-8(10)	11(8)	-17(10)
C(8B)	22(8)	39(11)	32(9)	-3(8)	1(6)	-2(7)
C(9B)	17(7)	31(10)	29(9)	-2(8)	5(6)	-11(7)
C(10B)	19(8)	41(11)	29(9)	-13(8)	-5(6)	-4(7)
C(1S)	59(11)	32(11)	25(9)	-9(8)	7(8)	-2(9)
Cl(1S)	49(3)	55(3)	47(3)	1(2)	-3(2)	3(2)
Cl(2S)	51(3)	60(3)	67(3)	-5(3)	-16(3)	5(3)
C(2S)	33(10)	63(15)	67(14)	-17(11)	20(9)	1(9)
Cl(3S)	60(3)	70(4)	57(3)	-2(3)	-9(2)	-3(3)
Cl(4S)	36(3)	61(3)	77(4)	-12(3)	6(2)	1(2)
C(3S)	49(12)	120(20)	29(11)	-3(13)	2(8)	24(12)
Cl(5S)	125(6)	86(5)	125(6)	-14(5)	-29(5)	6(5)
Cl(6S)	78(5)	273(14)	68(5)	-36(7)	7(4)	-82(7)

Table 5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **3a**

	x	y	z	U(eq)
H(12A)	-4669	-587	3042	43
H(13A)	-3394	-753	2375	56
H(14A)	-2504	-1937	2490	56
H(15A)	-2806	-2916	3245	61
H(16A)	-4108	-2773	3891	44
H(12B)	-5715	-1695	2599	45
H(13B)	-6951	-1798	1892	38
H(14B)	-8431	-1682	2304	45
H(15B)	-8667	-1599	3367	49
H(16B)	-7427	-1589	4059	35
H(21A)	-6231	664	4157	51
H(21B)	-6894	-127	4175	51
H(21C)	-6357	95	3549	51
H(31A)	-5414	884	5003	55
H(31B)	-4776	1072	4417	55
H(31C)	-4343	800	5071	55
H(41A)	-2796	-548	4899	67
H(41B)	-3262	157	4477	67
H(41C)	-3105	-762	4201	67
H(51A)	-3088	-2025	5024	60
H(51B)	-3822	-2558	5400	60
H(51C)	-3256	-1846	5750	60
H(62A)	-7288	-1645	5249	41
H(63A)	-8413	-767	5661	52
H(64A)	-8024	458	6174	53
H(65A)	-6466	812	6318	66
H(66A)	-5382	-109	5939	42
H(62B)	-4372	-1294	6476	40
H(63B)	-4323	-1732	7521	45
H(64B)	-5165	-2883	7851	41
H(65B)	-6052	-3643	7118	37
H(66B)	-6144	-3144	6091	33

H(2AA)	-4735	-4078	5804	48
H(3AA)	-3774	-5194	5716	33
H(5AA)	-3309	-6508	5164	49
H(6AA)	-3535	-7473	4394	43
H(7AA)	-4613	-7196	3589	47
H(8AA)	-5519	-6056	3657	41
H(2BA)	-7147	-3394	3052	36
H(3BA)	-8244	-4386	2933	41
H(5BA)	-8964	-5766	3222	48
H(6BA)	-8968	-6907	3828	52
H(7BA)	-7798	-7183	4553	58
H(8BA)	-6662	-6187	4679	38
H(1SA)	-5170	-3327	2884	46
H(1SB)	-4447	-3160	2342	46
H(2SA)	-1502	-4052	12845	65
H(2SB)	-2074	-4774	12509	65
H(3SA)	-4573	-1164	8716	81
H(3SB)	-4004	-932	9326	81