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Neutral dinuclear palladium(II) complex containing chiral *P,S*-bridging diamidophosphite-thioether ligands

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Experimental Section

General Remarks. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker Avance 600 (600 MHz for ^{1}H, 151 MHz, for $^{13}C\{^{1}H\}$, and 243 MHz for $^{31}P\{^{1}H\}$) or Bruker Avance 400 (400 MHz for ^{1}H) spectrometers. Chemical shifts are referenced to the residual solvent peak ($CHCl_3$: δ_H = 7.26 ppm) or to the solvent resonance ($CDCl_3$: δ_C = 77.16 ppm) as the internal standard, or to 85% H_3PO_4 as the external standard (δ_P = 0 ppm). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet, vt = virtual triplet), coupling constants (Hz), integration, and assignment.

X-ray Crystal Structure Data were collected on a STOE diffractometer with a Pilatus100K detector, focusing mirror collimation Mo Kα (0.7071Å) radiation, plane graphite monochromator, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing were performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences in the intensities of symmetry-equivalent reflections (multi-scan method). Structures were solved and refined with SHELX program.[S1] Nonhydrogen atoms were refined using the anisotropic full matrix least-square procedure. All hydrogen atoms were placed in the calculated positions and allowed to ride on their parent atoms [C–H 0.93–0.98 Å; U_{iso}(H) = 1.2 U_{eq}(C)]. Molecular geometry calculations (see Tables S1–S4) were performed using the SHELX program, and the molecular graphics were prepared using the DIAMOND software.[S2] CCDC 2207922 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

The HRMS spectrum was recorded using a quadrupole time-of-flight mass spectrometer TripleTOF 5600+ (AB Sciex, Concord, ON, Canada) equipped with the electrospray ionization source TurboIon Spray and the liquid chromatography system LC-30 «Nexera» (Shimadzu, Tokyo, Japan). Samples were injected directly into the ionization source in 0.2 μl portions and into 0.3 ml min^{-1} methanol flow without chromatographic separation. Ionization was performed in positive and negative modes. Overall scanning conditions corresponded to TOFMS.

IR spectra were recorded on a VERTEX 70v Fourier-transform IR spectrophotometer (Germany) by the attenuated total reflection (ATR) method using a Pike GladyATR adapter with a diamond crystal in the range 600-100 cm^{-1}, spectral resolution of 4 cm^{-1}. The spectra were obtained directly from powder samples without pretreatment. Measured ATR spectra were corrected using OPUS 7 software to allow for the wavelength dependence of radiation penetration depth into sample.

All reactions were carried out under a dry argon atmosphere in flame-dried glassware. *n*-Hexane and diethyl ether were distilled from sodium benzophenone ketyl prior to use; dichloromethane was distilled from CaH_2.

(1*R*,5*R*)-3-(4-Phenylthiobutoxy)-2,4-diphenyl-2,4-diaza-3-phosphabicyclo[3.4.0]nonane (**L**) was prepared as previously described.[S3]

Synthesis of $[Pd_2Cl_4L_2]$ complex (**1**). A solution of ligand **L** (74 mg, 0.15 mmol) and bis(acetonitrile)palladium dichloride (40 mg, 0.15 mmol) in dichloromethane (5 ml) was stirred for 1 h at room temperature under an argon atmosphere. The volatile materials were removed *in vacuo*. The residue was redissolved in CH_2Cl_2, and the solution was filtered through Celite. The filtrate was concentrated under reduced pressure to *ca*. 1 ml and added dropwise to vigorously stirred diethyl ether. The formed precipitate was separated from the mother liquor by centrifugation, washed with diethyl ether and dried *in vacuo* (0.05 mbar) providing complex **1** as a yellow powder (95 mg, 94%): m.p. 158°C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 1.25-1.89 (br.m; 24H), 2.32 (d; ^3J(H,H) = 12.0; 2H), 2.44 (d; ^3J(H,H) = 12.0; 2H), 3.55-3.63 (br.m; 4H), 4.05-4.12 (br.m; 4H), 7.06-7.10 (m; 6H), 7.23-7.36 (m; 16H), 7.59 (t, ^3J(H,H) = 7.6; 4H), 7.74 (d, ^3J(H,H) = 7.7; 4H) ppm. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 30°C): δ = 24.41 (s; CH_2), 24.46 (s; CH_2), 25.28 (s; $SCH_2\underline{C}H_2$), 27.90 (br.s; $OCH_2\underline{C}H_2$), 28.49 (br.s; $\underline{C}H_2CH$), 29.02 (s; $\underline{C}H_2CH$), 39.02 (s; SCH_2), 64.01 (s; CH), 65.17 (s; CH), 66.49 (vt, J(C,P) = 4.7; OCH_2), 121.51 (br.s; *o*-CH(Ph)), 122.41 (br.s; *o*-CH(Ph)), 123.10 (s; *p*-CH(Ph)), 123.86 (s; *p*-CH(Ph)), 129.12 (s; *m*-CH(Ph)), 129.53 (br.s; *m*-CH(Ph)), 129.58 (s; *p*-CH(Ph)), 129.77 (br.s; *m*-CH(Ph)), 130.05 (s; SC(Ph)), 132.05 (s; *o*-CH(Ph)), 139.87 (vt, J(C,P) = 2.4 Hz; NC(Ph)), 141.09 (vt, J(C,P) = 6.1 Hz; NC(Ph)) ppm. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$, 30°C): δ = 88.4 (s) ppm. ESI HRMS: m/z 1269.1250 $[M - Cl]^+$ (calculated 1269.1232 $[M - Cl]^+$), 1093.2839 $[M - Cl - PdCl_2]^+$ (calculated 1093.2820 $[M - Cl - PdCl_2]^+$), 617.0783 $[M - Cl - PdCl_2 - \mathbf{L}]^+$ (calculated 617.0769 $[M - Cl - PdCl_2 - \mathbf{L}]^+$), 581.1015 $[M - Cl - PdCl_2 - \mathbf{L} - HCl]^+$ (calculated 581.1002 $[M - Cl - PdCl_2 - \mathbf{L} - HCl]^+$).

Single crystals of the complex suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-hexane into a solution of **C** in CH_2Cl_2.

References

S1. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

S2. K. Brandenburg, DIAMOND, Release 2.1d; Crystal Impact GbR: Bonn, Germany, 2000.

S3. I. V. Chuchelkin, K. N. Gavrilov, V. K. Gavrilov, S. V. Zheglov, I. D. Firsin, A. M. Perepukhov, A. V. Maximychev, N. E. Borisova, I. A. Zamilatskov, V. S. Tyurin, C. Dejoie, V. V. Chernyshev, V. S. Zimarev and N. S. Goulioukina, *Organometallics*, 2021, **40**, 3645.

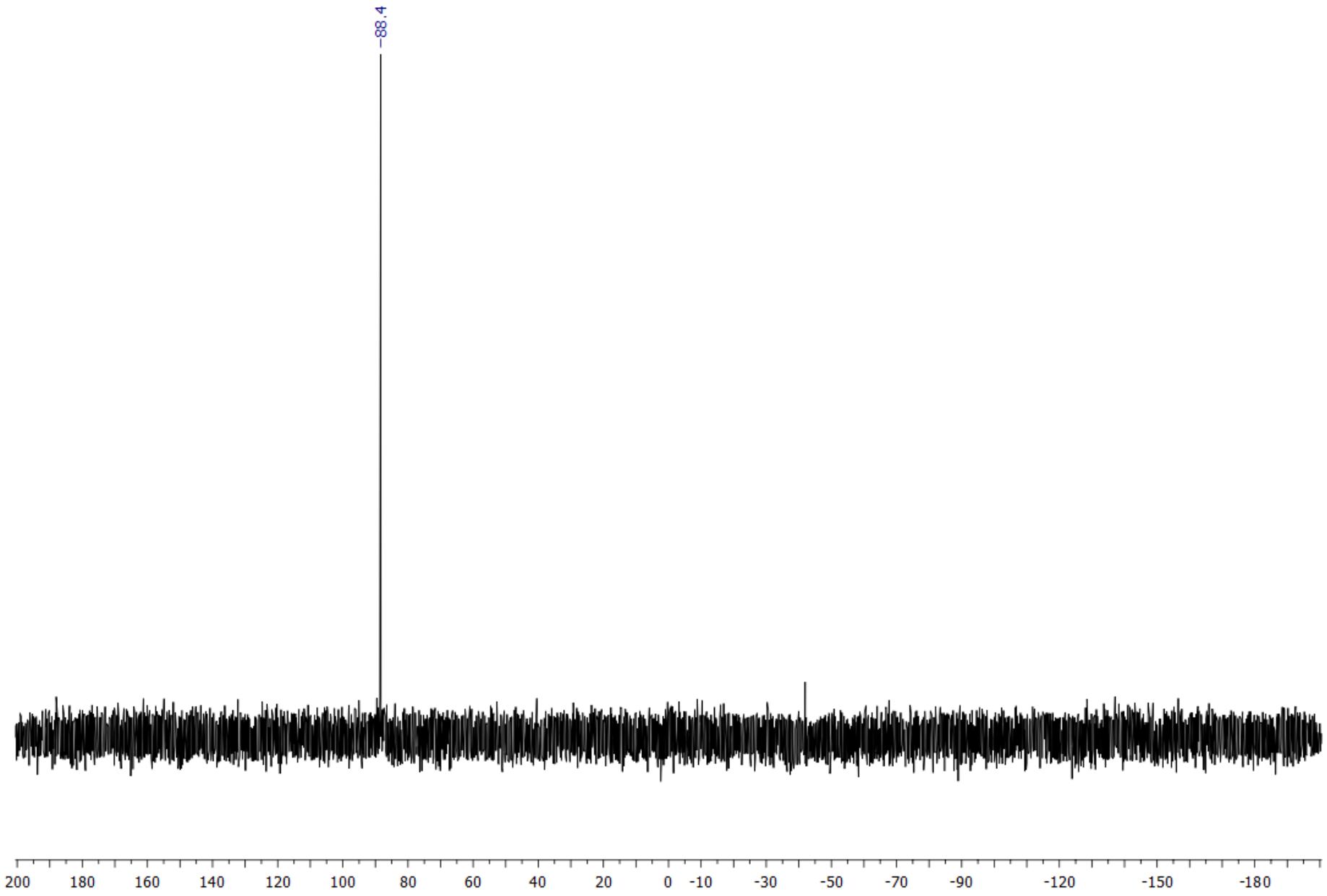

Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum of **1**

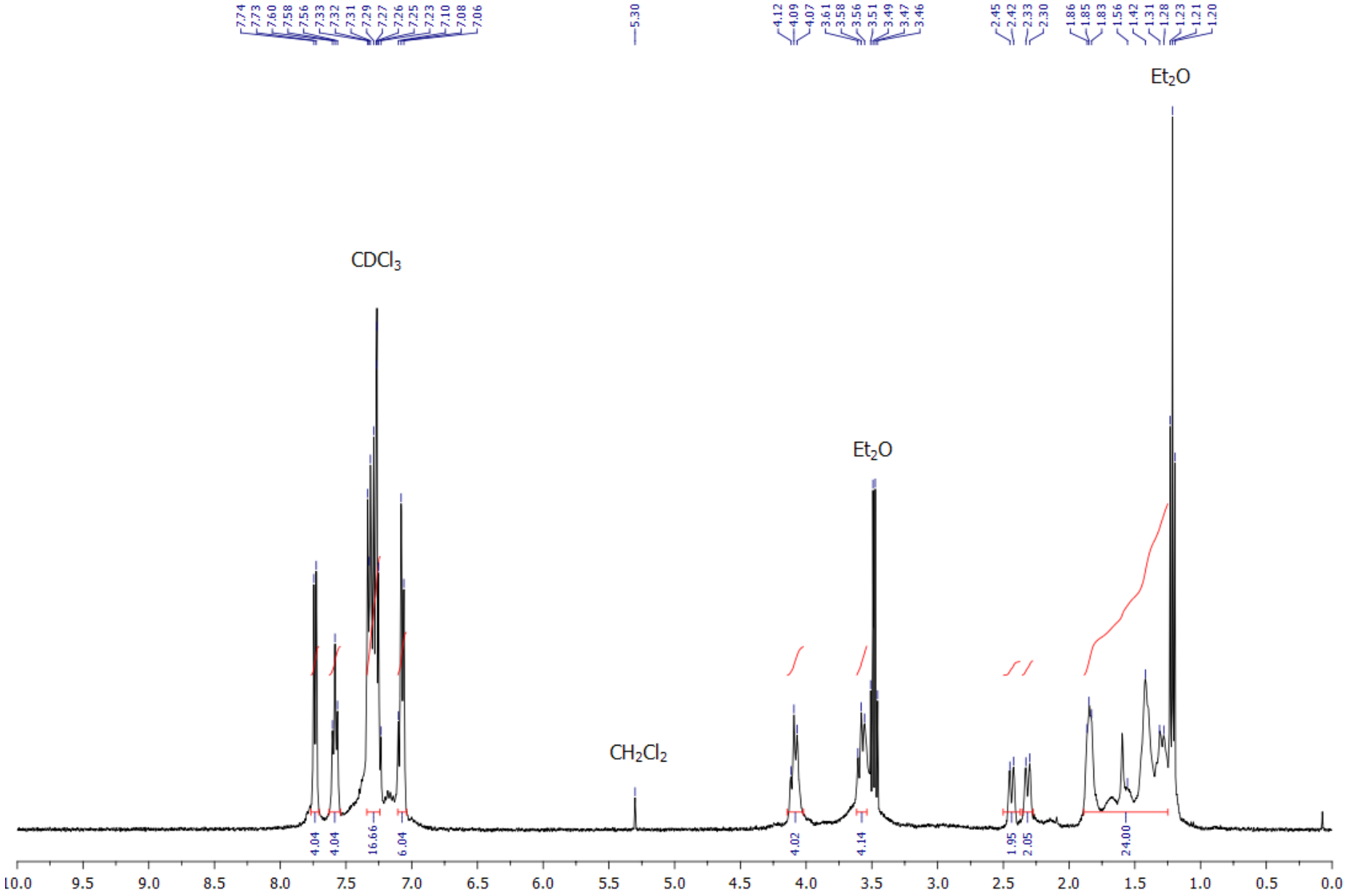

Figure S2. ^{1}H NMR spectrum of **1**

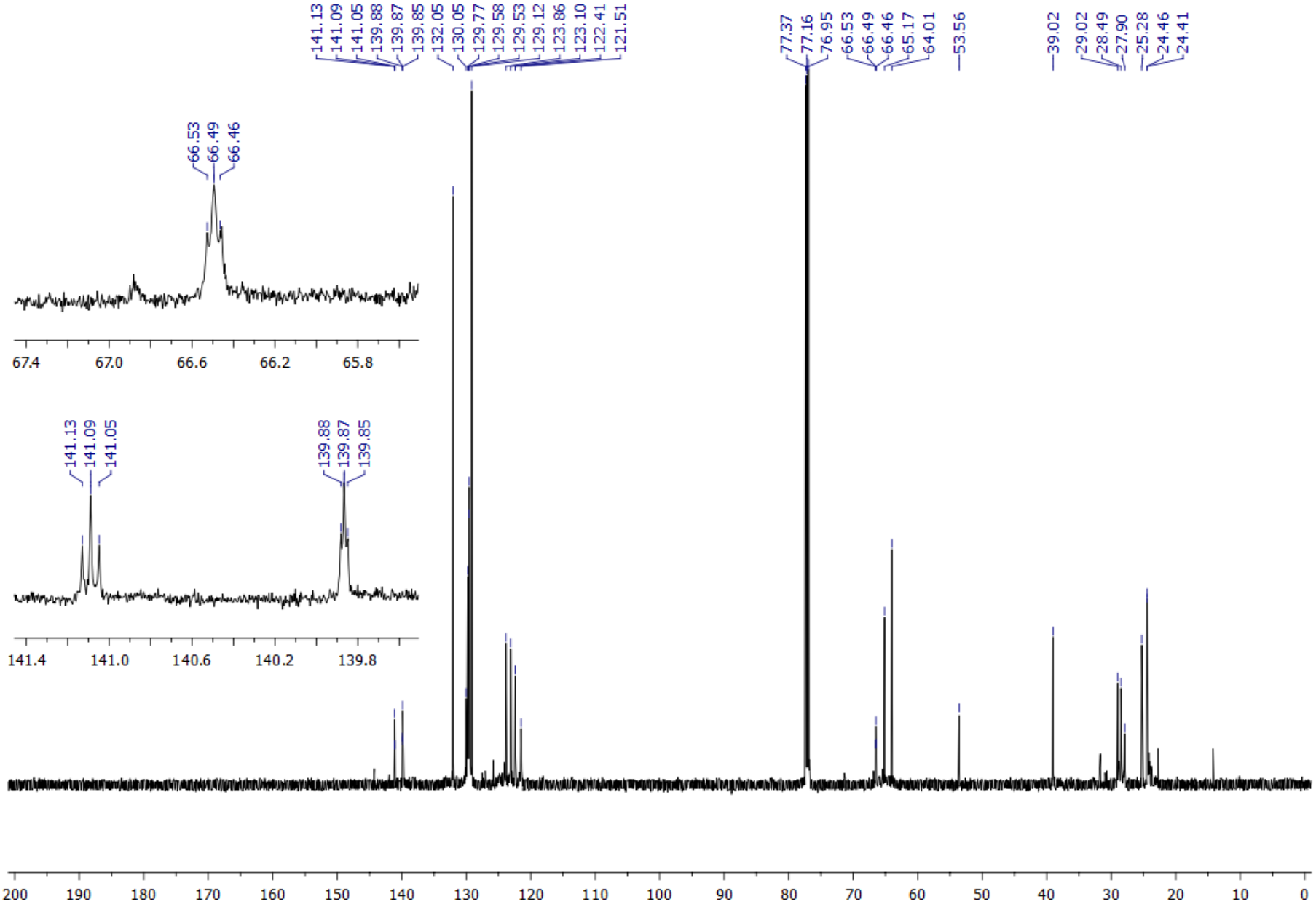

Figure S3. $^{13}C\{^{1}H\}$ spectrum of **1**

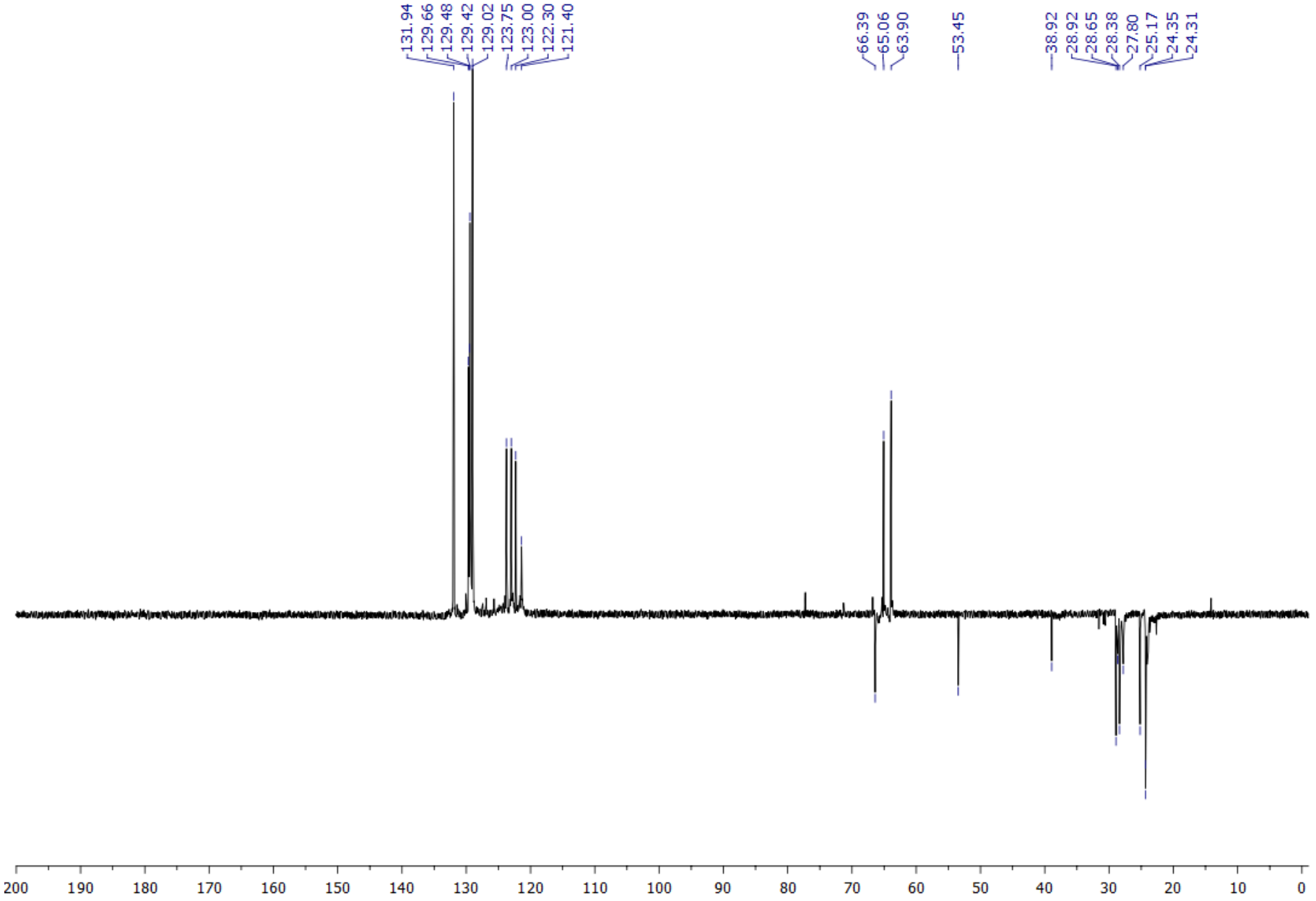

Figure S4. $^{13}C\{^{1}H\}$ DEPT NMR spectrum of **1**

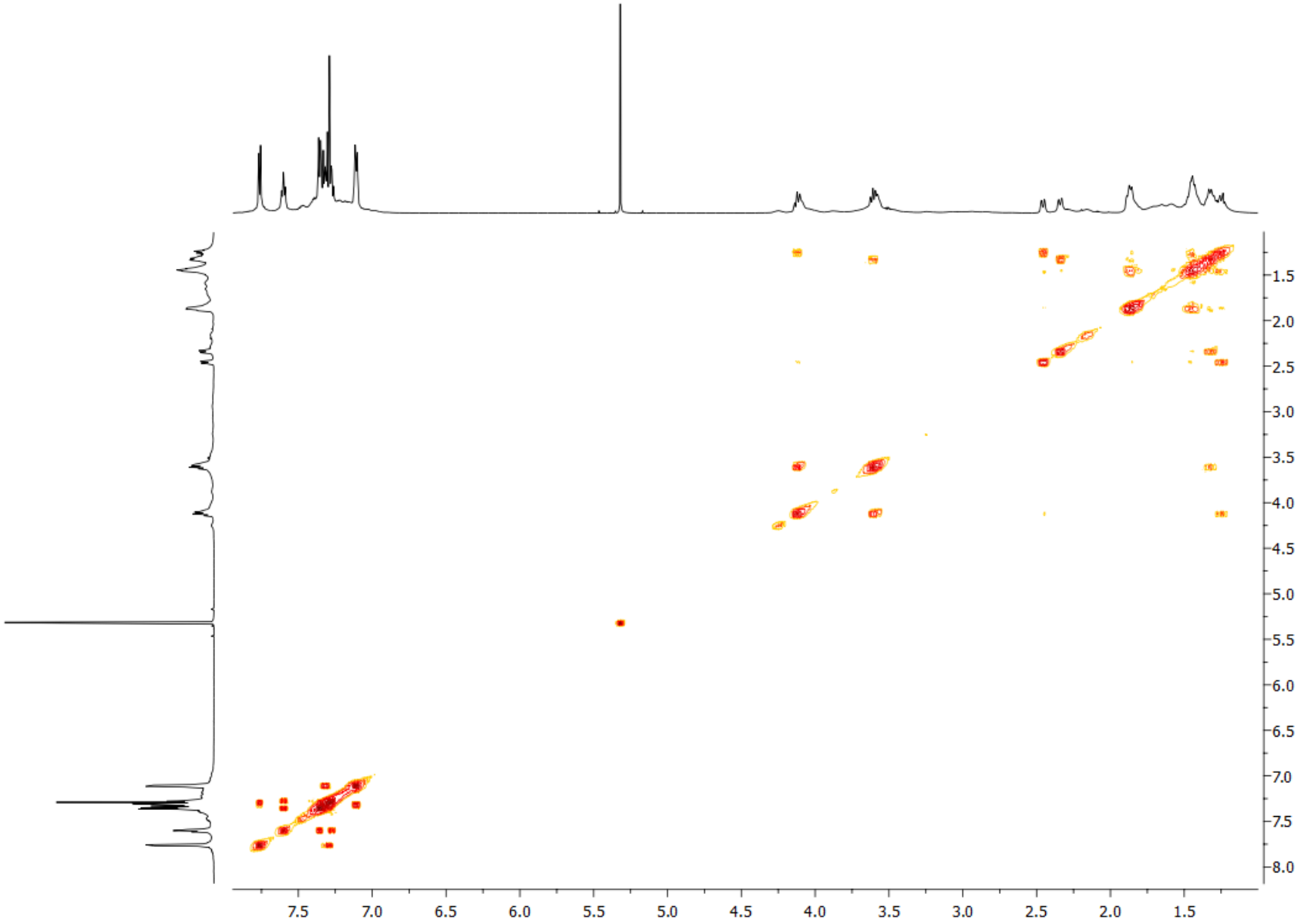

Figure S5. ^{1}H-^{1}H-COSY NMR spectrum of **1**

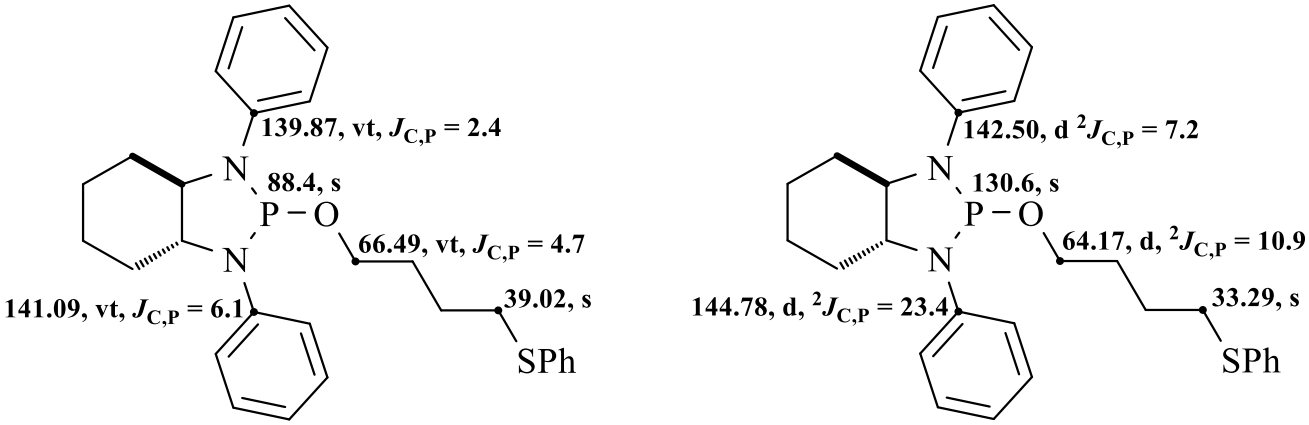

Figure S6. $^{31}P\{^1H\}$ NMR and selected $^{13}C\{^1H\}$ NMR chemical shifts for coordinated (left) and uncoordinated[S3] (right) ligand **L**.

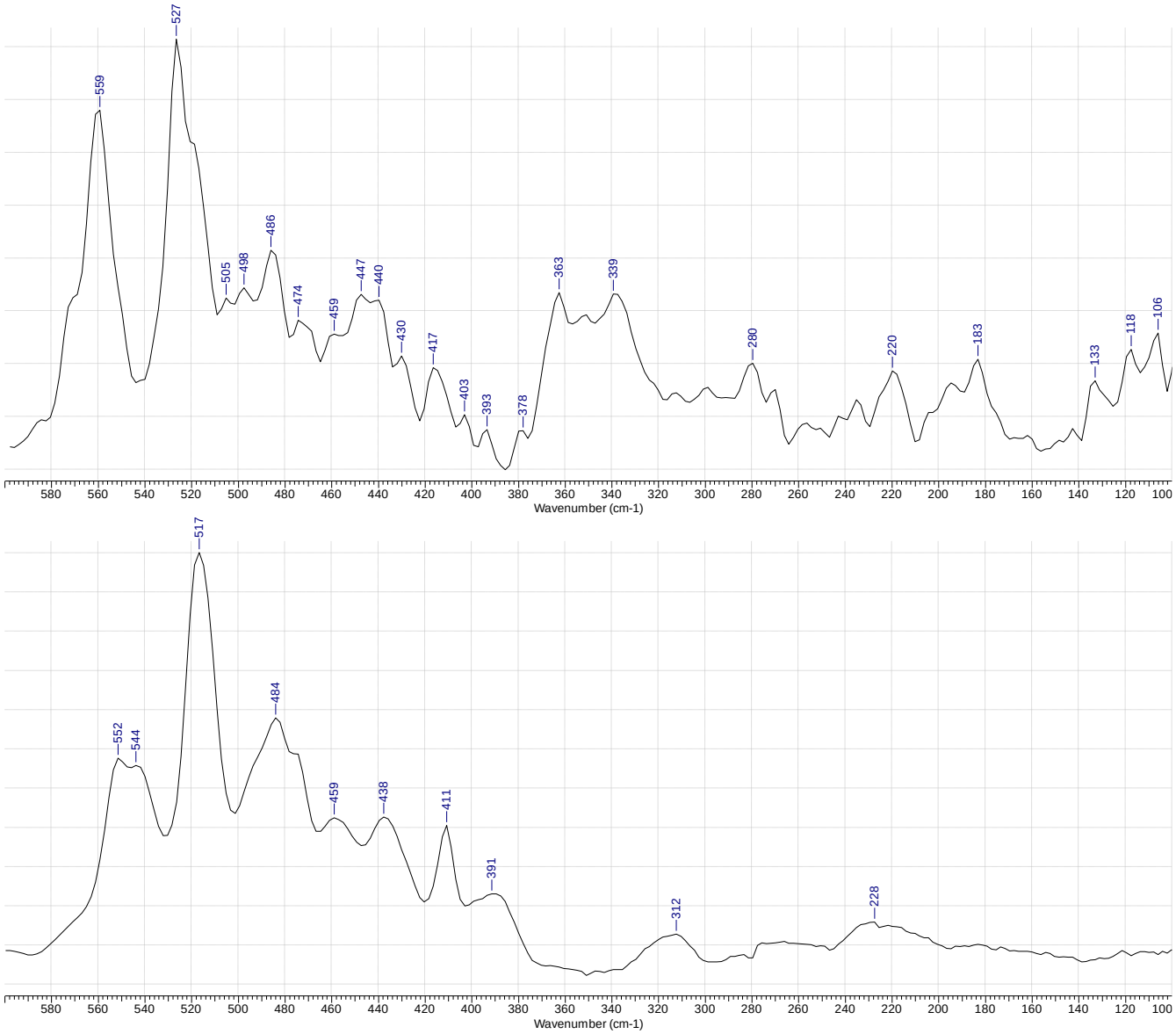

Figure S7. Far infrared ATR spectra of complex **1** (top) and ligand **L** (bottom)

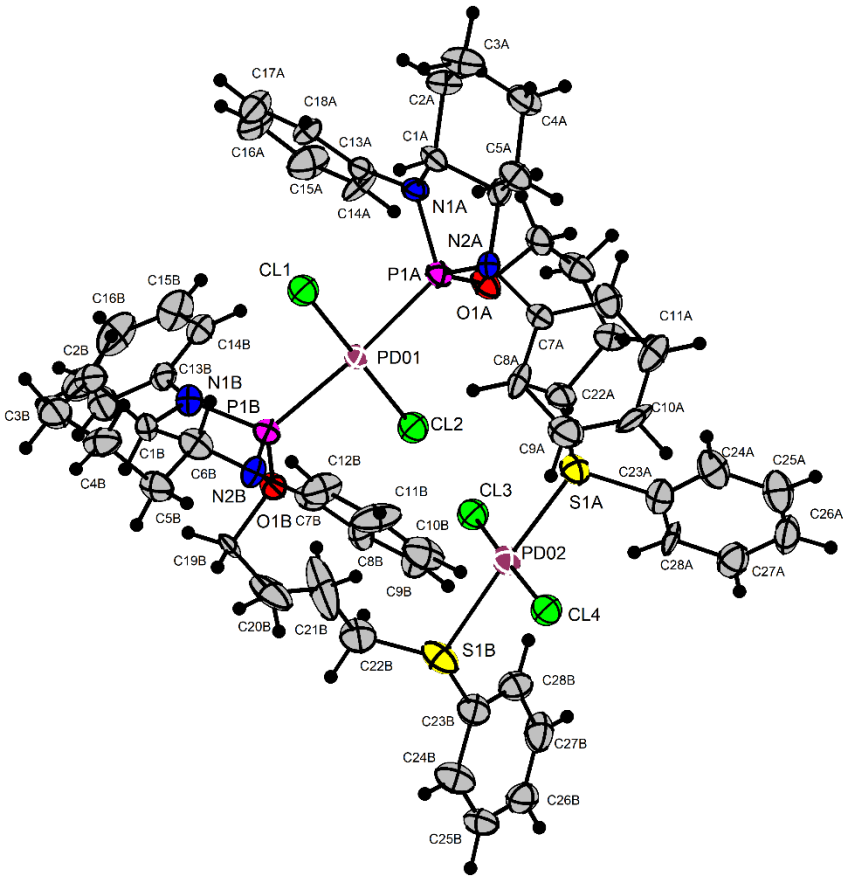

Figure S8. Molecular structure of **1**. Solvate molecules of CH_2Cl_2 are omitted for clarity.

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

Identification code	shelx	
Empirical formula	C56 H66 Cl4 N4 O2 P2 Pd2 S2	
Formula weight	1307.88	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 13.4740(5) Å	α= 90°.
	b = 18.0706(7) Å	β= 115.850(4)°.
	c = 14.6689(8) Å	γ = 90°.
Volume	3214.2(3) $Å^3$	
Z	4	
Density (calculated)	1.527 Mg/m^3	
Absorption coefficient	1.050 mm^{-1}	
F(000)	1504	
Theta range for data collection	2.023 to 26.999°.	
Index ranges	-17<=h<=17, -23<=k<=22, -18<=l<=18	
Reflections collected	81543	
Independent reflections	13224 [R(int) = 0.2244]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13224 / 1 / 703	
Goodness-of-fit on F^2	0.849	
Final R indices [I>2sigma(I)]	R1 = 0.0791, wR2 = 0.1622	
R indices (all data)	R1 = 0.2409, wR2 = 0.2211	
Absolute structure parameter	0.05(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.655 and -0.879 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **1**.

Pd(01)-Cl(2)	2.263(5)
Pd(01)-P(1B)	2.294(6)
Pd(01)-P(1A)	2.301(6)
Pd(01)-Cl(1)	2.310(5)
Pd(02)-Cl(3)	2.290(8)
Pd(02)-Cl(4)	2.307(8)
Pd(02)-S(1B)	2.323(6)
Pd(02)-S(1A)	2.325(6)
P(1A)-O(1A)	1.591(15)
P(1A)-N(2A)	1.682(17)
P(1A)-N(1A)	1.728(18)
S(1A)-C(22A)	1.79(3)
S(1A)-C(23A)	1.81(2)
O(1A)-C(19A)	1.42(2)
N(1A)-C(13A)	1.39(3)
N(1A)-C(1A)	1.45(2)
N(2A)-C(7A)	1.45(3)
N(2A)-C(6A)	1.48(3)
C(1A)-C(6A)	1.50(3)
C(1A)-C(2A)	1.50(3)
C(1A)-H(1A)	0.9800
C(2A)-C(3A)	1.54(3)
C(2A)-H(2A1)	0.9700
C(2A)-H(2A2)	0.9700
C(3A)-C(4A)	1.53(4)
C(3A)-H(3A1)	0.9700
C(3A)-H(3A2)	0.9700
C(4A)-C(5A)	1.51(3)
C(4A)-H(4A1)	0.9700
C(4A)-H(4A2)	0.9700
C(5A)-C(6A)	1.53(3)
C(5A)-H(5A1)	0.9700
C(5A)-H(5A2)	0.9700
C(6A)-H(6A)	0.9800
C(7A)-C(8A)	1.35(3)
C(7A)-C(12A)	1.36(3)
C(8A)-C(9A)	1.37(4)
C(8A)-H(8A)	0.9300
C(9A)-C(10A)	1.37(4)
C(9A)-H(9A)	0.9300
C(10A)-C(11A)	1.35(4)
C(10A)-H(10A)	0.9300
C(11A)-C(12A)	1.39(3)
C(11A)-H(11A)	0.9300
C(12A)-H(12A)	0.9300
C(13A)-C(18A)	1.38(3)
C(13A)-C(14A)	1.42(3)
C(14A)-C(15A)	1.35(3)
C(14A)-H(14A)	0.9300
C(15A)-C(16A)	1.40(4)
C(15A)-H(15A)	0.9300
C(16A)-C(17A)	1.33(3)
C(16A)-H(16A)	0.9300
C(17A)-C(18A)	1.42(3)
C(17A)-H(17A)	0.9300
C(18A)-H(18A)	0.9300
C(19A)-C(20A)	1.43(3)
C(19A)-H(19A)	0.9700
C(19A)-H(19B)	0.9700
C(20A)-C(21A)	1.53(3)
C(20A)-H(20A)	0.9700
C(20A)-H(20B)	0.9700
C(21A)-C(22A)	1.56(3)
C(21A)-H(21A)	0.9700

C(21A)-H(21B)	0.9700
C(22A)-H(22A)	0.9700
C(22A)-H(22B)	0.9700
C(23A)-C(24A)	1.37(3)
C(23A)-C(28A)	1.39(3)
C(24A)-C(25A)	1.39(4)
C(24A)-H(24A)	0.9300
C(25A)-C(26A)	1.33(4)
C(25A)-H(25A)	0.9300
C(26A)-C(27A)	1.38(4)
C(26A)-H(26A)	0.9300
C(27A)-C(28A)	1.32(3)
C(27A)-H(27A)	0.9300
C(28A)-H(28A)	0.9300
P(1B)-O(1B)	1.588(13)
P(1B)-N(1B)	1.649(19)
P(1B)-N(2B)	1.681(18)
S(1B)-C(23B)	1.80(2)
S(1B)-C(22B)	1.81(3)
O(1B)-C(19B)	1.47(2)
N(1B)-C(13B)	1.44(3)
N(1B)-C(1B)	1.45(3)
N(2B)-C(7B)	1.40(3)
N(2B)-C(6B)	1.45(3)
C(1B)-C(6B)	1.53(3)
C(1B)-C(2B)	1.55(3)
C(1B)-H(1B)	0.9800
C(2B)-C(3B)	1.49(4)
C(2B)-H(2B1)	0.9700
C(2B)-H(2B2)	0.9700
C(3B)-C(4B)	1.53(4)
C(3B)-H(3B1)	0.9700
C(3B)-H(3B2)	0.9700
C(4B)-C(5B)	1.50(3)
C(4B)-H(4B1)	0.9700
C(4B)-H(4B2)	0.9700
C(5B)-C(6B)	1.50(3)
C(5B)-H(5B1)	0.9700
C(5B)-H(5B2)	0.9700
C(6B)-H(6B)	0.9800
C(7B)-C(12B)	1.39(3)
C(7B)-C(8B)	1.40(3)
C(8B)-C(9B)	1.38(3)
C(8B)-H(8B)	0.9300
C(9B)-C(10B)	1.39(4)
C(9B)-H(9B)	0.9300
C(10B)-C(11B)	1.35(4)
C(10B)-H(10B)	0.9300
C(11B)-C(12B)	1.38(4)
C(11B)-H(11B)	0.9300
C(12B)-H(12B)	0.9300
C(13B)-C(14B)	1.38(3)
C(13B)-C(18B)	1.41(3)
C(14B)-C(15B)	1.41(3)
C(14B)-H(14B)	0.9300
C(15B)-C(16B)	1.35(4)
C(15B)-H(15B)	0.9300
C(16B)-C(17B)	1.40(4)
C(16B)-H(16B)	0.9300
C(17B)-C(18B)	1.35(4)
C(17B)-H(17B)	0.9300
C(18B)-H(18B)	0.9300
C(19B)-C(20B)	1.49(3)
C(19B)-H(19C)	0.9700
C(19B)-H(19D)	0.9700
C(20B)-C(21B)	1.17(4)

C(20B)-H(20C)	0.9700
C(20B)-H(20D)	0.9700
C(21B)-C(22B)	1.46(3)
C(21B)-H(21C)	0.9700
C(21B)-H(21D)	0.9700
C(22B)-H(22C)	0.9700
C(22B)-H(22D)	0.9700
C(23B)-C(28B)	1.33(3)
C(23B)-C(24B)	1.39(3)
C(24B)-C(25B)	1.37(4)
C(24B)-H(24B)	0.9300
C(25B)-C(26B)	1.33(4)
C(25B)-H(25B)	0.9300
C(26B)-C(27B)	1.33(4)
C(26B)-H(26B)	0.9300
C(27B)-C(28B)	1.40(3)
C(27B)-H(27B)	0.9300
C(28B)-H(28B)	0.9300
C(29)-Cl(5)	1.57(4)
C(29)-Cl(6)	1.85(4)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-Cl(8)	1.67(3)
C(30)-Cl(7)	1.73(4)
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700

Cl(2)-Pd(01)-P(1B)	91.3(2)
Cl(2)-Pd(01)-P(1A)	92.5(2)
P(1B)-Pd(01)-P(1A)	175.4(2)
Cl(2)-Pd(01)-Cl(1)	173.9(3)
P(1B)-Pd(01)-Cl(1)	88.5(2)
P(1A)-Pd(01)-Cl(1)	88.0(2)
Cl(3)-Pd(02)-Cl(4)	176.2(3)
Cl(3)-Pd(02)-S(1B)	93.3(3)
Cl(4)-Pd(02)-S(1B)	86.9(3)
Cl(3)-Pd(02)-S(1A)	95.9(2)
Cl(4)-Pd(02)-S(1A)	84.0(2)
S(1B)-Pd(02)-S(1A)	170.6(3)
O(1A)-P(1A)-N(2A)	109.2(8)
O(1A)-P(1A)-N(1A)	106.0(9)
N(2A)-P(1A)-N(1A)	92.7(8)
O(1A)-P(1A)-Pd(01)	111.9(5)
N(2A)-P(1A)-Pd(01)	116.3(7)
N(1A)-P(1A)-Pd(01)	118.8(6)
C(22A)-S(1A)-C(23A)	103.7(11)
C(22A)-S(1A)-Pd(02)	111.7(7)
C(23A)-S(1A)-Pd(02)	103.9(8)
C(19A)-O(1A)-P(1A)	125.9(12)
C(13A)-N(1A)-C(1A)	124.3(18)
C(13A)-N(1A)-P(1A)	119.3(12)
C(1A)-N(1A)-P(1A)	109.8(14)
C(7A)-N(2A)-C(6A)	122.1(15)
C(7A)-N(2A)-P(1A)	118.7(13)
C(6A)-N(2A)-P(1A)	110.6(14)
N(1A)-C(1A)-C(6A)	105.0(17)
N(1A)-C(1A)-C(2A)	115.6(18)
C(6A)-C(1A)-C(2A)	108.7(17)
N(1A)-C(1A)-H(1A)	109.1
C(6A)-C(1A)-H(1A)	109.1
C(2A)-C(1A)-H(1A)	109.1
C(1A)-C(2A)-C(3A)	106.6(19)
C(1A)-C(2A)-H(2A1)	110.4
C(3A)-C(2A)-H(2A1)	110.4
C(1A)-C(2A)-H(2A2)	110.4
C(3A)-C(2A)-H(2A2)	110.4

H(2A1)-C(2A)-H(2A2)	108.6
C(4A)-C(3A)-C(2A)	113(2)
C(4A)-C(3A)-H(3A1)	109.0
C(2A)-C(3A)-H(3A1)	109.0
C(4A)-C(3A)-H(3A2)	109.0
C(2A)-C(3A)-H(3A2)	109.0
H(3A1)-C(3A)-H(3A2)	107.8
C(5A)-C(4A)-C(3A)	112(2)
C(5A)-C(4A)-H(4A1)	109.2
C(3A)-C(4A)-H(4A1)	109.2
C(5A)-C(4A)-H(4A2)	109.2
C(3A)-C(4A)-H(4A2)	109.2
H(4A1)-C(4A)-H(4A2)	107.9
C(4A)-C(5A)-C(6A)	108(2)
C(4A)-C(5A)-H(5A1)	110.2
C(6A)-C(5A)-H(5A1)	110.2
C(4A)-C(5A)-H(5A2)	110.2
C(6A)-C(5A)-H(5A2)	110.2
H(5A1)-C(5A)-H(5A2)	108.5
N(2A)-C(6A)-C(1A)	104.1(15)
N(2A)-C(6A)-C(5A)	115(2)
C(1A)-C(6A)-C(5A)	109.1(17)
N(2A)-C(6A)-H(6A)	109.6
C(1A)-C(6A)-H(6A)	109.6
C(5A)-C(6A)-H(6A)	109.6
C(8A)-C(7A)-C(12A)	121(2)
C(8A)-C(7A)-N(2A)	118.5(19)
C(12A)-C(7A)-N(2A)	121(2)
C(7A)-C(8A)-C(9A)	121(2)
C(7A)-C(8A)-H(8A)	119.5
C(9A)-C(8A)-H(8A)	119.5
C(10A)-C(9A)-C(8A)	120(3)
C(10A)-C(9A)-H(9A)	119.9
C(8A)-C(9A)-H(9A)	119.9
C(11A)-C(10A)-C(9A)	118(3)
C(11A)-C(10A)-H(10A)	121.0
C(9A)-C(10A)-H(10A)	121.0
C(10A)-C(11A)-C(12A)	123(3)
C(10A)-C(11A)-H(11A)	118.7
C(12A)-C(11A)-H(11A)	118.7
C(7A)-C(12A)-C(11A)	118(3)
C(7A)-C(12A)-H(12A)	121.1
C(11A)-C(12A)-H(12A)	121.1
C(18A)-C(13A)-N(1A)	122(2)
C(18A)-C(13A)-C(14A)	118(2)
N(1A)-C(13A)-C(14A)	120(2)
C(15A)-C(14A)-C(13A)	119(2)
C(15A)-C(14A)-H(14A)	120.3
C(13A)-C(14A)-H(14A)	120.3
C(14A)-C(15A)-C(16A)	122(3)
C(14A)-C(15A)-H(15A)	118.9
C(16A)-C(15A)-H(15A)	118.9
C(17A)-C(16A)-C(15A)	119(2)
C(17A)-C(16A)-H(16A)	120.4
C(15A)-C(16A)-H(16A)	120.4
C(16A)-C(17A)-C(18A)	121(3)
C(16A)-C(17A)-H(17A)	119.6
C(18A)-C(17A)-H(17A)	119.6
C(13A)-C(18A)-C(17A)	120(2)
C(13A)-C(18A)-H(18A)	119.9
C(17A)-C(18A)-H(18A)	119.9
O(1A)-C(19A)-C(20A)	111.8(17)
O(1A)-C(19A)-H(19A)	109.3
C(20A)-C(19A)-H(19A)	109.3
O(1A)-C(19A)-H(19B)	109.3
C(20A)-C(19A)-H(19B)	109.3

H(19A)-C(19A)-H(19B)	107.9
C(19A)-C(20A)-C(21A)	115(2)
C(19A)-C(20A)-H(20A)	108.5
C(21A)-C(20A)-H(20A)	108.5
C(19A)-C(20A)-H(20B)	108.5
C(21A)-C(20A)-H(20B)	108.5
H(20A)-C(20A)-H(20B)	107.5
C(20A)-C(21A)-C(22A)	111(2)
C(20A)-C(21A)-H(21A)	109.5
C(22A)-C(21A)-H(21A)	109.5
C(20A)-C(21A)-H(21B)	109.5
C(22A)-C(21A)-H(21B)	109.5
H(21A)-C(21A)-H(21B)	108.1
C(21A)-C(22A)-S(1A)	112.1(17)
C(21A)-C(22A)-H(22A)	109.2
S(1A)-C(22A)-H(22A)	109.2
C(21A)-C(22A)-H(22B)	109.2
S(1A)-C(22A)-H(22B)	109.2
H(22A)-C(22A)-H(22B)	107.9
C(24A)-C(23A)-C(28A)	120(2)
C(24A)-C(23A)-S(1A)	118(2)
C(28A)-C(23A)-S(1A)	121.0(17)
C(23A)-C(24A)-C(25A)	117(3)
C(23A)-C(24A)-H(24A)	121.6
C(25A)-C(24A)-H(24A)	121.6
C(26A)-C(25A)-C(24A)	121(3)
C(26A)-C(25A)-H(25A)	119.5
C(24A)-C(25A)-H(25A)	119.5
C(25A)-C(26A)-C(27A)	122(3)
C(25A)-C(26A)-H(26A)	119.1
C(27A)-C(26A)-H(26A)	119.1
C(28A)-C(27A)-C(26A)	118(2)
C(28A)-C(27A)-H(27A)	121.1
C(26A)-C(27A)-H(27A)	121.1
C(27A)-C(28A)-C(23A)	122(2)
C(27A)-C(28A)-H(28A)	119.2
C(23A)-C(28A)-H(28A)	119.2
O(1B)-P(1B)-N(1B)	108.6(8)
O(1B)-P(1B)-N(2B)	109.6(8)
N(1B)-P(1B)-N(2B)	92.0(9)
O(1B)-P(1B)-Pd(01)	109.0(5)
N(1B)-P(1B)-Pd(01)	118.0(7)
N(2B)-P(1B)-Pd(01)	118.4(6)
C(23B)-S(1B)-C(22B)	100.7(11)
C(23B)-S(1B)-Pd(02)	110.4(9)
C(22B)-S(1B)-Pd(02)	110.7(10)
C(19B)-O(1B)-P(1B)	127.1(12)
C(13B)-N(1B)-C(1B)	123.9(16)
C(13B)-N(1B)-P(1B)	116.8(14)
C(1B)-N(1B)-P(1B)	113.4(15)
C(7B)-N(2B)-C(6B)	121.4(17)
C(7B)-N(2B)-P(1B)	117.6(15)
C(6B)-N(2B)-P(1B)	112.2(14)
N(1B)-C(1B)-C(6B)	104.6(16)
N(1B)-C(1B)-C(2B)	115.9(18)
C(6B)-C(1B)-C(2B)	109.3(18)
N(1B)-C(1B)-H(1B)	108.9
C(6B)-C(1B)-H(1B)	108.9
C(2B)-C(1B)-H(1B)	108.9
C(3B)-C(2B)-C(1B)	109(2)
C(3B)-C(2B)-H(2B1)	109.9
C(1B)-C(2B)-H(2B1)	109.9
C(3B)-C(2B)-H(2B2)	109.9
C(1B)-C(2B)-H(2B2)	109.9
H(2B1)-C(2B)-H(2B2)	108.3
C(2B)-C(3B)-C(4B)	113(2)

C(2B)-C(3B)-H(3B1)	108.9
C(4B)-C(3B)-H(3B1)	108.9
C(2B)-C(3B)-H(3B2)	108.9
C(4B)-C(3B)-H(3B2)	108.9
H(3B1)-C(3B)-H(3B2)	107.7
C(5B)-C(4B)-C(3B)	113(2)
C(5B)-C(4B)-H(4B1)	109.0
C(3B)-C(4B)-H(4B1)	109.0
C(5B)-C(4B)-H(4B2)	109.0
C(3B)-C(4B)-H(4B2)	109.0
H(4B1)-C(4B)-H(4B2)	107.8
C(6B)-C(5B)-C(4B)	108(2)
C(6B)-C(5B)-H(5B1)	110.1
C(4B)-C(5B)-H(5B1)	110.1
C(6B)-C(5B)-H(5B2)	110.1
C(4B)-C(5B)-H(5B2)	110.1
H(5B1)-C(5B)-H(5B2)	108.4
N(2B)-C(6B)-C(5B)	121(2)
N(2B)-C(6B)-C(1B)	102.1(16)
C(5B)-C(6B)-C(1B)	106(2)
N(2B)-C(6B)-H(6B)	109.0
C(5B)-C(6B)-H(6B)	109.0
C(1B)-C(6B)-H(6B)	109.0
C(12B)-C(7B)-C(8B)	115(2)
C(12B)-C(7B)-N(2B)	124(2)
C(8B)-C(7B)-N(2B)	121.2(19)
C(9B)-C(8B)-C(7B)	122(2)
C(9B)-C(8B)-H(8B)	119.0
C(7B)-C(8B)-H(8B)	119.0
C(8B)-C(9B)-C(10B)	120(3)
C(8B)-C(9B)-H(9B)	119.9
C(10B)-C(9B)-H(9B)	119.9
C(11B)-C(10B)-C(9B)	119(3)
C(11B)-C(10B)-H(10B)	120.4
C(9B)-C(10B)-H(10B)	120.4
C(10B)-C(11B)-C(12B)	120(3)
C(10B)-C(11B)-H(11B)	120.0
C(12B)-C(11B)-H(11B)	120.0
C(11B)-C(12B)-C(7B)	123(3)
C(11B)-C(12B)-H(12B)	118.5
C(7B)-C(12B)-H(12B)	118.5
C(14B)-C(13B)-C(18B)	119(2)
C(14B)-C(13B)-N(1B)	119(2)
C(18B)-C(13B)-N(1B)	121(2)
C(13B)-C(14B)-C(15B)	117(2)
C(13B)-C(14B)-H(14B)	121.3
C(15B)-C(14B)-H(14B)	121.3
C(16B)-C(15B)-C(14B)	123(3)
C(16B)-C(15B)-H(15B)	118.4
C(14B)-C(15B)-H(15B)	118.4
C(15B)-C(16B)-C(17B)	119(3)
C(15B)-C(16B)-H(16B)	120.7
C(17B)-C(16B)-H(16B)	120.7
C(18B)-C(17B)-C(16B)	119(3)
C(18B)-C(17B)-H(17B)	120.3
C(16B)-C(17B)-H(17B)	120.3
C(17B)-C(18B)-C(13B)	122(3)
C(17B)-C(18B)-H(18B)	119.0
C(13B)-C(18B)-H(18B)	119.0
O(1B)-C(19B)-C(20B)	104.9(17)
O(1B)-C(19B)-H(19C)	110.8
C(20B)-C(19B)-H(19C)	110.8
O(1B)-C(19B)-H(19D)	110.8
C(20B)-C(19B)-H(19D)	110.8
H(19C)-C(19B)-H(19D)	108.8
C(21B)-C(20B)-C(19B)	135(3)

C(21B)-C(20B)-H(20C)	103.3
C(19B)-C(20B)-H(20C)	103.3
C(21B)-C(20B)-H(20D)	103.3
C(19B)-C(20B)-H(20D)	103.3
H(20C)-C(20B)-H(20D)	105.2
C(20B)-C(21B)-C(22B)	132(3)
C(20B)-C(21B)-H(21C)	104.2
C(22B)-C(21B)-H(21C)	104.2
C(20B)-C(21B)-H(21D)	104.2
C(22B)-C(21B)-H(21D)	104.2
H(21C)-C(21B)-H(21D)	105.5
C(21B)-C(22B)-S(1B)	111(3)
C(21B)-C(22B)-H(22C)	109.5
S(1B)-C(22B)-H(22C)	109.5
C(21B)-C(22B)-H(22D)	109.5
S(1B)-C(22B)-H(22D)	109.5
H(22C)-C(22B)-H(22D)	108.1
C(28B)-C(23B)-C(24B)	121(2)
C(28B)-C(23B)-S(1B)	123(2)
C(24B)-C(23B)-S(1B)	116(2)
C(25B)-C(24B)-C(23B)	120(3)
C(25B)-C(24B)-H(24B)	120.2
C(23B)-C(24B)-H(24B)	120.2
C(26B)-C(25B)-C(24B)	120(3)
C(26B)-C(25B)-H(25B)	120.2
C(24B)-C(25B)-H(25B)	120.2
C(27B)-C(26B)-C(25B)	121(3)
C(27B)-C(26B)-H(26B)	119.7
C(25B)-C(26B)-H(26B)	119.7
C(26B)-C(27B)-C(28B)	122(3)
C(26B)-C(27B)-H(27B)	119.0
C(28B)-C(27B)-H(27B)	119.0
C(23B)-C(28B)-C(27B)	117(3)
C(23B)-C(28B)-H(28B)	121.5
C(27B)-C(28B)-H(28B)	121.5
Cl(5)-C(29)-Cl(6)	114.7(17)
Cl(5)-C(29)-H(29A)	108.6
Cl(6)-C(29)-H(29A)	108.6
Cl(5)-C(29)-H(29B)	108.6
Cl(6)-C(29)-H(29B)	108.6
H(29A)-C(29)-H(29B)	107.6
Cl(8)-C(30)-Cl(7)	115(2)
Cl(8)-C(30)-H(30A)	108.5
Cl(7)-C(30)-H(30A)	108.5
Cl(8)-C(30)-H(30B)	108.5
Cl(7)-C(30)-H(30B)	108.5
H(30A)-C(30)-H(30B)	107.5

Table S3. Torsion angles [°] for **1**.

N(2A)-P(1A)-O(1A)-C(19A)	-52(2)
N(1A)-P(1A)-O(1A)-C(19A)	46(2)
Pd(01)-P(1A)-O(1A)-C(19A)	177.4(17)
O(1A)-P(1A)-N(1A)-C(13A)	82.6(17)
N(2A)-P(1A)-N(1A)-C(13A)	-166.5(16)
Pd(01)-P(1A)-N(1A)-C(13A)	-44.4(18)
O(1A)-P(1A)-N(1A)-C(1A)	-124.6(14)
N(2A)-P(1A)-N(1A)-C(1A)	-13.6(14)
Pd(01)-P(1A)-N(1A)-C(1A)	108.5(12)
O(1A)-P(1A)-N(2A)-C(7A)	-53.7(17)
N(1A)-P(1A)-N(2A)-C(7A)	-161.7(15)
Pd(01)-P(1A)-N(2A)-C(7A)	74.2(16)
O(1A)-P(1A)-N(2A)-C(6A)	94.8(14)
N(1A)-P(1A)-N(2A)-C(6A)	-13.2(14)
Pd(01)-P(1A)-N(2A)-C(6A)	-137.3(12)
C(13A)-N(1A)-C(1A)-C(6A)	-173.3(19)
P(1A)-N(1A)-C(1A)-C(6A)	35.5(19)
C(13A)-N(1A)-C(1A)-C(2A)	-54(3)
P(1A)-N(1A)-C(1A)-C(2A)	155.2(17)
N(1A)-C(1A)-C(2A)-C(3A)	179(2)
C(6A)-C(1A)-C(2A)-C(3A)	-63(2)
C(1A)-C(2A)-C(3A)-C(4A)	55(3)
C(2A)-C(3A)-C(4A)-C(5A)	-52(3)
C(3A)-C(4A)-C(5A)-C(6A)	54(3)
C(7A)-N(2A)-C(6A)-C(1A)	-177.8(18)
P(1A)-N(2A)-C(6A)-C(1A)	35.0(19)
C(7A)-N(2A)-C(6A)-C(5A)	-59(3)
P(1A)-N(2A)-C(6A)-C(5A)	154.1(16)
N(1A)-C(1A)-C(6A)-N(2A)	-43(2)
C(2A)-C(1A)-C(6A)-N(2A)	-167.6(17)
N(1A)-C(1A)-C(6A)-C(5A)	-166.4(17)
C(2A)-C(1A)-C(6A)-C(5A)	69(2)
C(4A)-C(5A)-C(6A)-N(2A)	-179.1(19)
C(4A)-C(5A)-C(6A)-C(1A)	-63(2)
C(6A)-N(2A)-C(7A)-C(8A)	151.9(19)
P(1A)-N(2A)-C(7A)-C(8A)	-63(2)
C(6A)-N(2A)-C(7A)-C(12A)	-31(3)
P(1A)-N(2A)-C(7A)-C(12A)	114.1(19)
C(12A)-C(7A)-C(8A)-C(9A)	-1(3)
N(2A)-C(7A)-C(8A)-C(9A)	176(2)
C(7A)-C(8A)-C(9A)-C(10A)	-1(4)
C(8A)-C(9A)-C(10A)-C(11A)	2(4)
C(9A)-C(10A)-C(11A)-C(12A)	-2(4)
C(8A)-C(7A)-C(12A)-C(11A)	1(3)
N(2A)-C(7A)-C(12A)-C(11A)	-176(2)
C(10A)-C(11A)-C(12A)-C(7A)	0(4)
C(1A)-N(1A)-C(13A)-C(18A)	-20(3)
P(1A)-N(1A)-C(13A)-C(18A)	128.3(19)
C(1A)-N(1A)-C(13A)-C(14A)	159.0(19)
P(1A)-N(1A)-C(13A)-C(14A)	-52(3)
C(18A)-C(13A)-C(14A)-C(15A)	2(4)
N(1A)-C(13A)-C(14A)-C(15A)	-177(2)
C(13A)-C(14A)-C(15A)-C(16A)	0(4)
C(14A)-C(15A)-C(16A)-C(17A)	-2(5)
C(15A)-C(16A)-C(17A)-C(18A)	0(4)
N(1A)-C(13A)-C(18A)-C(17A)	176(2)
C(14A)-C(13A)-C(18A)-C(17A)	-4(3)
C(16A)-C(17A)-C(18A)-C(13A)	3(4)
P(1A)-O(1A)-C(19A)-C(20A)	172.6(17)
O(1A)-C(19A)-C(20A)-C(21A)	-61(3)

C(19A)-C(20A)-C(21A)-C(22A)	89(3)
C(20A)-C(21A)-C(22A)-S(1A)	-148.9(18)
C(23A)-S(1A)-C(22A)-C(21A)	-63.9(18)
Pd(02)-S(1A)-C(22A)-C(21A)	-175.3(14)
C(22A)-S(1A)-C(23A)-C(24A)	89(2)
Pd(02)-S(1A)-C(23A)-C(24A)	-155(2)
C(22A)-S(1A)-C(23A)-C(28A)	-85(2)
Pd(02)-S(1A)-C(23A)-C(28A)	32(2)
C(28A)-C(23A)-C(24A)-C(25A)	-7(4)
S(1A)-C(23A)-C(24A)-C(25A)	179(2)
C(23A)-C(24A)-C(25A)-C(26A)	5(5)
C(24A)-C(25A)-C(26A)-C(27A)	-2(5)
C(25A)-C(26A)-C(27A)-C(28A)	2(4)
C(26A)-C(27A)-C(28A)-C(23A)	-5(4)
C(24A)-C(23A)-C(28A)-C(27A)	8(4)
S(1A)-C(23A)-C(28A)-C(27A)	-179(2)
N(1B)-P(1B)-O(1B)-C(19B)	-54.6(19)
N(2B)-P(1B)-O(1B)-C(19B)	44.5(19)
Pd(01)-P(1B)-O(1B)-C(19B)	175.6(15)
O(1B)-P(1B)-N(1B)-C(13B)	-49.9(17)
N(2B)-P(1B)-N(1B)-C(13B)	-161.3(15)
Pd(01)-P(1B)-N(1B)-C(13B)	74.8(15)
O(1B)-P(1B)-N(1B)-C(1B)	104.1(14)
N(2B)-P(1B)-N(1B)-C(1B)	-7.3(14)
Pd(01)-P(1B)-N(1B)-C(1B)	-131.2(12)
O(1B)-P(1B)-N(2B)-C(7B)	82.5(15)
N(1B)-P(1B)-N(2B)-C(7B)	-166.9(15)
Pd(01)-P(1B)-N(2B)-C(7B)	-43.4(16)
O(1B)-P(1B)-N(2B)-C(6B)	-129.6(13)
N(1B)-P(1B)-N(2B)-C(6B)	-19.0(14)
Pd(01)-P(1B)-N(2B)-C(6B)	104.5(13)
C(13B)-N(1B)-C(1B)-C(6B)	-178.9(18)
P(1B)-N(1B)-C(1B)-C(6B)	29.2(19)
C(13B)-N(1B)-C(1B)-C(2B)	-59(3)
P(1B)-N(1B)-C(1B)-C(2B)	149.6(15)
N(1B)-C(1B)-C(2B)-C(3B)	-177(2)
C(6B)-C(1B)-C(2B)-C(3B)	-59(3)
C(1B)-C(2B)-C(3B)-C(4B)	49(3)
C(2B)-C(3B)-C(4B)-C(5B)	-50(3)
C(3B)-C(4B)-C(5B)-C(6B)	58(3)
C(7B)-N(2B)-C(6B)-C(5B)	-59(3)
P(1B)-N(2B)-C(6B)-C(5B)	154.2(17)
C(7B)-N(2B)-C(6B)-C(1B)	-176.5(17)
P(1B)-N(2B)-C(6B)-C(1B)	37.0(19)
C(4B)-C(5B)-C(6B)-N(2B)	178.4(19)
C(4B)-C(5B)-C(6B)-C(1B)	-66(2)
N(1B)-C(1B)-C(6B)-N(2B)	-40(2)
C(2B)-C(1B)-C(6B)-N(2B)	-164.3(17)
N(1B)-C(1B)-C(6B)-C(5B)	-167.1(17)
C(2B)-C(1B)-C(6B)-C(5B)	68(2)
C(6B)-N(2B)-C(7B)-C(12B)	-11(3)
P(1B)-N(2B)-C(7B)-C(12B)	133.4(19)
C(6B)-N(2B)-C(7B)-C(8B)	171(2)
P(1B)-N(2B)-C(7B)-C(8B)	-44(2)
C(12B)-C(7B)-C(8B)-C(9B)	5(3)
N(2B)-C(7B)-C(8B)-C(9B)	-178(2)
C(7B)-C(8B)-C(9B)-C(10B)	-2(4)
C(8B)-C(9B)-C(10B)-C(11B)	0(4)
C(9B)-C(10B)-C(11B)-C(12B)	-2(5)
C(10B)-C(11B)-C(12B)-C(7B)	5(5)
C(8B)-C(7B)-C(12B)-C(11B)	-6(4)
N(2B)-C(7B)-C(12B)-C(11B)	176(3)
C(1B)-N(1B)-C(13B)-C(14B)	155(2)

P(1B)-N(1B)-C(13B)-C(14B)	-54(2)
C(1B)-N(1B)-C(13B)-C(18B)	-29(3)
P(1B)-N(1B)-C(13B)-C(18B)	122(2)
C(18B)-C(13B)-C(14B)-C(15B)	0(3)
N(1B)-C(13B)-C(14B)-C(15B)	176(2)
C(13B)-C(14B)-C(15B)-C(16B)	3(4)
C(14B)-C(15B)-C(16B)-C(17B)	-5(5)
C(15B)-C(16B)-C(17B)-C(18B)	5(5)
C(16B)-C(17B)-C(18B)-C(13B)	-3(4)
C(14B)-C(13B)-C(18B)-C(17B)	0(4)
N(1B)-C(13B)-C(18B)-C(17B)	-176(2)
P(1B)-O(1B)-C(19B)-C(20B)	-159(2)
O(1B)-C(19B)-C(20B)-C(21B)	-11(8)
C(19B)-C(20B)-C(21B)-C(22B)	-175(5)
C(20B)-C(21B)-C(22B)-S(1B)	-118(8)
C(23B)-S(1B)-C(22B)-C(21B)	-176(3)
Pd(02)-S(1B)-C(22B)-C(21B)	-59(3)
C(22B)-S(1B)-C(23B)-C(28B)	97(3)
Pd(02)-S(1B)-C(23B)-C(28B)	-20(3)
C(22B)-S(1B)-C(23B)-C(24B)	-85(2)
Pd(02)-S(1B)-C(23B)-C(24B)	158.5(17)
C(28B)-C(23B)-C(24B)-C(25B)	2(4)
S(1B)-C(23B)-C(24B)-C(25B)	-177(2)
C(23B)-C(24B)-C(25B)-C(26B)	-3(4)
C(24B)-C(25B)-C(26B)-C(27B)	1(4)
C(25B)-C(26B)-C(27B)-C(28B)	1(4)
C(24B)-C(23B)-C(28B)-C(27B)	0(4)
S(1B)-C(23B)-C(28B)-C(27B)	179(2)
C(26B)-C(27B)-C(28B)-C(23B)	-2(4)

Table S4. Hydrogen bonds for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1A)-H(1A)...Cl(5)#1	0.98	2.88	3.77(2)	151.2
C(14A)-H(14A)...O(1A)	0.93	2.61	3.27(3)	128.0
C(18A)-H(18A)...Cl(5)#1	0.93	2.98	3.89(3)	164.1
C(22A)-H(22B)...O(1A)	0.97	2.46	3.09(3)	122.0
C(22A)-H(22B)...Cl(2)	0.97	2.66	3.38(2)	131.6
C(8B)-H(8B)...O(1B)	0.93	2.58	3.27(3)	131.1
C(22B)-H(22C)...Cl(3)	0.97	2.93	3.44(3)	114.6
C(28B)-H(28B)...Cl(3)	0.93	2.76	3.51(3)	138.4
C(29)-H(29B)...S(1B)	0.97	3.02	3.74(3)	132.8
C(29)-H(29B)...Cl(4)	0.97	2.74	3.67(4)	160.2
C(30)-H(30A)...Cl(2)	0.97	2.96	3.48(3)	114.4
C(30)-H(30A)...Cl(3)	0.97	2.73	3.61(4)	151.1

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1