Electronic Supplementary Information

First paramagnetic Pd^{II} complex with a PdN_4S_2 coordination core

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Physical measurements: Infrared spectra (Nujol) were recorded with a Thermo Nicolet 380 FT-IR spectrometer in the range 400–4000 cm^{-1}. NMR spectra ($CDCl_3$) were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. Magnetization of powdered samples was measured between 2 and 300 K on a MPMS-5 Quantum Design magnetometer. Ball-milling was performed using steel balls in a SPEX SamplePrep 8000M Mixer/Mill. Elemental analysis was performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments.

Synthesis of [Pd{2-PyNHC(S)NP(S)(OiPr)$_2$-1,5-S,S'}$_2$] ([Pd(L-1,5-S,S')$_2$]) and [Pd{2-PyNHC(S)NP(S)(OiPr)$_2$-1,5,7-N,N',S}$_2$] ([Pd(L-1,5,7-N,N',S)$_2$]): A suspension of **HL** (0.667 g, 2 mmol) in aqueous methanol (20 mL) was mixed with a methanol solution of potassium hydroxide (0.123 g, 2.2 mmol). An aqueous (20 mL) solution of $PdCl_2$ (0.177 g, 1 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for 3 h and left overnight. The resulting complex was extracted with dichloromethane, washed with water and dried with anhydrous $MgSO_4$. The solvent was then removed in vacuo. The residue was extracted by *n*-hexane. A hexane insoluble deposit was recrystallized from a dichloromethane/*n*-hexane mixture, and orange crystals of **[Pd(L-1,5-*S*,*S*')$_2$]** were isolated. At the solvent-removal stage (*n*-hexane soluble), product **[Pd(L-1,5,7-*N*,*N*',*S*)$_2$]** was isolated as a blue powder.

[Pd(L-1,5-*S*,*S*')$_2$]: Yield: 0.625 g (81 %). IR ν (cm^{-1}): 564 (P=S), 978 (POC), 1294 (C=S), 1527 (SCN), 3251 (NH). ^{1}H NMR δ (ppm): 1.39 (d, $^3J_{H,H}$ = 6.2 Hz, 12H, CH_3, *i*Pr), 1.42 (d, $^3J_{H,H}$ = 6.2 Hz, 6H, CH_3, *i*Pr), 1.43 (d, $^3J_{H,H}$ = 6.1 Hz, 6H, CH_3, *i*Pr), 4.90 (d. sept, $^3J_{POCH}$ = 10.2 Hz, $^3J_{H,H}$ = 6.1 Hz, 4H, OCH), 6.92–7.01 (m, 2H, Py), 7.55–7.67 (m, 2H, Py), 8.13–8.20 (m, 2H, Py), 8.24–8.32 (m, 2H, Py), 8.43 (br. d, $^4J_{PNCNH}$ = 8.4 Hz, 1H, arylNH), 8.46 (br. d, $^4J_{PNCNH}$ = 8.4 Hz, 1H, arylNH); ^{31}P{^{1}H} NMR δ (ppm): 51.5 (1.5P), 51.9 (1P). $C_{24}H_{38}N_6O_4P_2PdS_4$ (771.21): calcd. C 37.38, H 4.97, N 10.90; found: C 37.23, H 4.90, N 10.99 %.

[Pd(L-1,5,7-*N*,*N*',*S*)$_2$]: Yield: 0.054 g (7 %). IR ν (cm^{-1}): 582 (P=S), 993 (POC), 1338 (C=S), 1547 (SCN), 3218 (NH). ^{1}H NMR δ (ppm): 0–3 (m, 36H, CH_3 + CH + Py, *i*Pr + Py), 19.4 (br. s, 2H, arylNH); ^{31}P{^{1}H} NMR δ (ppm): 76.6. $C_{24}H_{38}N_6O_4P_2PdS_4$ (771.21): calcd. C 37.38, H 4.97, N 10.90; found: C 37.51, H 4.92, N 10.81 %.

***Mechanically induced solid-state synthesis of [Pd(L-1,5,7-N,N',S)$_2$]*:** The potassium salt **KL** (0.742 g, 2 mmol), which was obtained similar as described previously,[1] and $PdCl_2$ (0.177 g, 1 mmol) were ball-milled for 48 hours. Then the obtained blue powder was extensively treated with H_2O (3 × 30 mL) and filtered. The solid material was then washed by *n*-hexane (5 × 50 mL) and dried in vacuum. The resulting product was analyzed by elemental analysis, IR and NMR spectroscopy. The obtained data testifies to the formation of the complex **[Pd(L-1,5,7-**

N,N',S)$_2$] with the isolated yield 0.409 g (53%). The recrystallization of the powder complex **[Pd(L-1,5,7-N,N',S)$_2$]** from a CH_2Cl_2/*n*-hexane mixture (1:3, v/v) gives the X-ray suitable crystals of the complex **[Pd(L-1,5-*S*,*S*')$_2$]**.

X-Ray crystallography: The X-ray diffraction data were collected on a STOE IPDS-II diffractometer. The images were indexed, integrated and scaled using the X-Area package.[2] Data were corrected for absorption using the PLATON program.[3] The structures were solved by direct methods using the SHELXS[3] program and refined first isotropically and then anisotropically using SHELXL97.[4] Hydrogen atoms were revealed from $\Delta\rho$ maps and refined using a riding model. All figures were generated using the program Mercury.[5]

CCDC 864257 contains the supplementary crystallographic data for **[Pd(L-1,5-*S*,*S*')$_2$]**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

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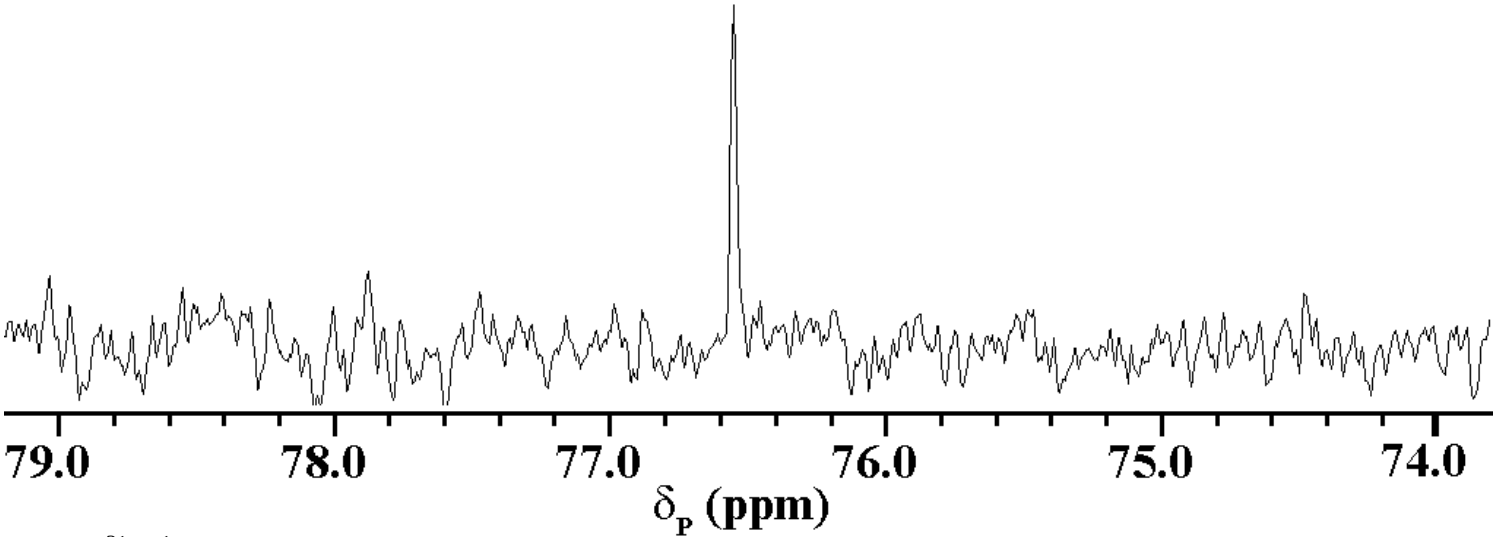

Fig. S1 $^{31}P\{^{1}H\}$ NMR spectrum of **[Pd(L-1,5,7-*N*,*N*′,*S*)$_2$]** in $CDCl_3$.

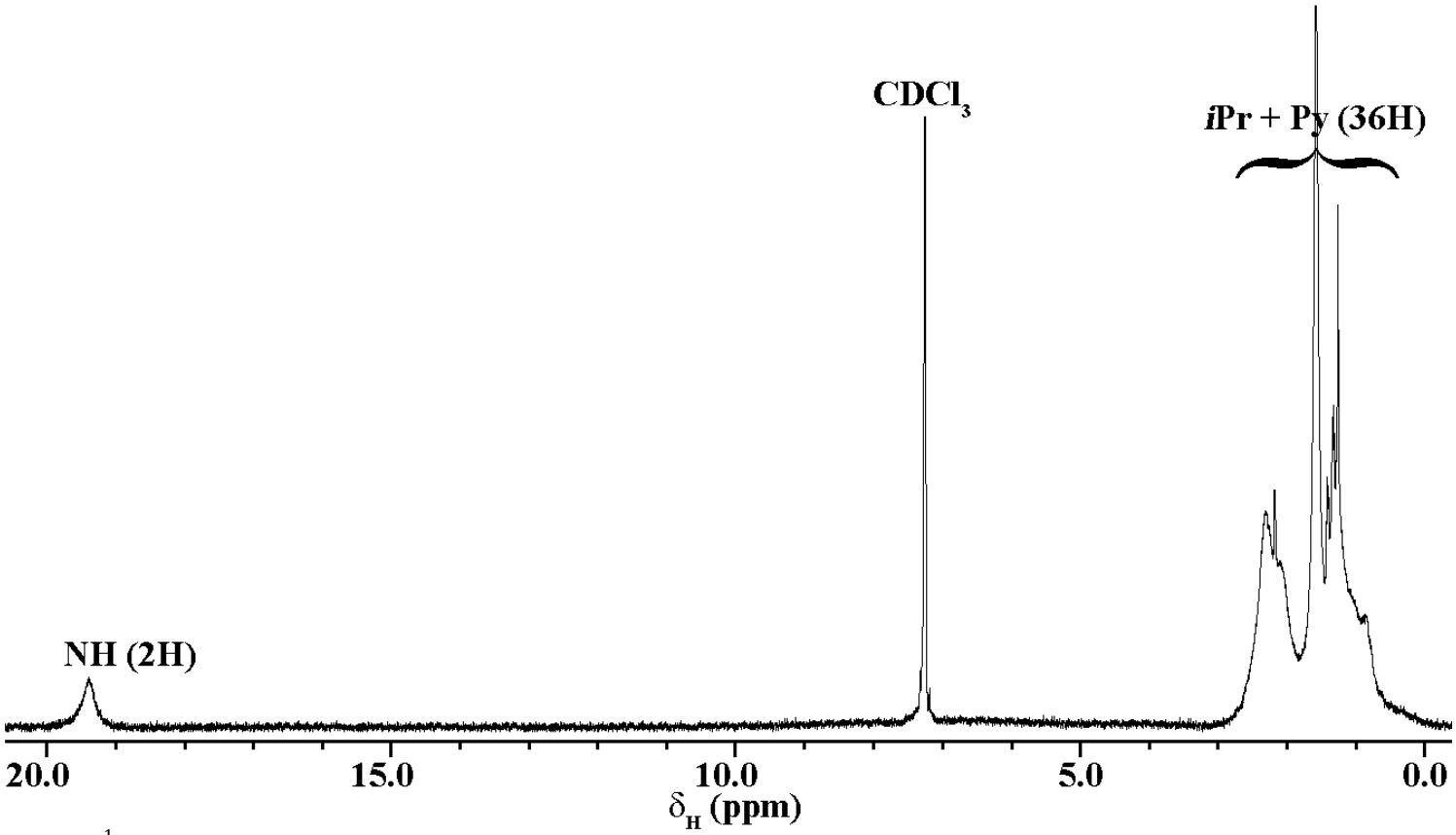

Fig. S2 ^{1}H NMR spectrum of **[Pd(L-1,5,7-*N*,*N*′,*S*)$_2$]** in $CDCl_3$.

Table S1. Crystal data, data collection and refinement details for **[Pd(L-1,5-*S*,*S*′)$_2$]**[a]

Empirical formula	$C_{24}H_{38}N_6O_4P_2PdS_4$
Formula weight	771.18
Temperature (*K*)	173(2)
Crystal system	triclinic
Space group	*P*–1
a (Å)	7.9596(12)
b (Å)	10.4276(15)
c (Å)	11.7207(18)
α (°)	112.870(9)
β (°)	94.830(9)
γ (°)	107.321(6)
V (Å^3)	833.3(2)
Z	1
D_{calc} (Mg m^{-3})	1.537
μ (mm^{-1})	0.943
F(000)	396
Recording range, θ_{max} (°)	2.8–30.5
Number of recorded reflections	20545
Number of recorded independent reflections	5080 (R_{int} = 0.049)
R indices (all data)	R_1 = 0.0363, wR_2 = 0.0709

[a] Measurements were made using Mo-K$_\alpha$ with λ = 0.71073 (Å).

Table S2. Selected bond lengths (Å) and bond angles (°) for **[Pd(L-1,5-*S*,*S*′)$_2$]**

Bond lengths			
Pd(1)–S(1)	2.3322(7)	P(1)–O(1)	1.5665(18)
Pd(1)–S(2)	2.3046(7)	P(1)–O(2)	1.5630(17)
N(1)–C(1)	1.301(3)	S(1)–P(1)	1.9958(8)
N(2)–C(1)	1.364(3)	S(2)–C(1)	1.738(2)
P(1)–N(1)	1.5934(19)		
Bond angles			
Pd(1)–S(1)–P(1)	95.86(3)	O(2)–P(1)–N(1)	107.29(9)
Pd(1)–S(2)–C(1)	115.05(8)	P(1)–N(1)–C(1)	128.52(15)
S(1)–Pd(1)–S(2)	97.93(2)	S(1)–P(1)–N(1)	117.62(8)
S(1)–Pd(1)–S(1)a	180.00	S(1)–P(1)–O(1)	113.32(6)
S(1)–Pd(1)–S(2)a	82.07(2)	S(1)–P(1)–O(2)	108.95(7)
N(1)–C(1)–N(2)	119.72(19)	S(2)–C(1)–N(1)	128.84(16)
O(1)–P(1)–O(2)	103.02(10)	S(2)–C(1)–N(2)	111.43(17)
O(1)–P(1)–N(1)	105.51(10)		
Torsion angles			
N(1)–P(1)–S(1)–Pd(1)	66.74(8)	O(2)–P(1)–(1)–C(1)	–166.0(2)
O(1)–P(1)–S(1)–Pd(1)	–56.92(8)	P(1)–N(1)–C(1)–N(2)	179.74(18)
O(2)–P(1)–S(1)–Pd(1)	–170.97(7)	P(1)–N(1)–C(1)–S(2)	–1.4(3)
O(1)–P(1)–N(1)–(1)	84.7(2)	S(1)–P(1)–N(1)–C(1)	–42.9(2)

Table S3. Hydrogen bond and hydrogen contact lengths (Å) and angles (°) for **[Pd(L-1,5-*S*,*S*′)$_2$]**[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(2)–H(2)···N(12)#1	0.85(3)	2.52(3)	3.356(3)	168(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 2 – *x*, –*y*, 1 – *z*.