

# Unique Pt<sub>5</sub> metallacycle: [Pt<sup>II</sup>Cl(pyrrolidinedithiocarbamate)]<sub>5</sub> †

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## Electronic Supplementary Information

### Instrumental and Synthesis:

Elemental analyses were carried out on a Fisons EA1108 CHNS-O microanalyser. IR spectra were recorded on Nicolet 5SXC FT-IR and 20F Far-IR spectrometers, as either Nujol mulls between KBr and polyethylene discs or as KBr pellets. Thermogravimetric data in air were obtained on Netzsch STA 449 thermoanalytical equipment (flux rate, 50 cm<sup>3</sup> min<sup>-1</sup>; heating rate, 5 °C min<sup>-1</sup>; and ref. material Al<sub>2</sub>O<sub>3</sub>). The weight of the samples in the crucible was about 15-25 mg.

PtCl<sub>2</sub>, PPh<sub>3</sub> and all the solvents were of commercial origin. PyDTM was synthesized as previously reported.<sup>S1</sup>

[PtCl<sub>2</sub>(PyDTM)] (**1**) was prepared by adding PtCl<sub>2</sub> (1.46 mmol) to a PyDTM solution in dichloromethane (1.60 mmol in 7 mL) with vigorous stirring (18 h). A red solution of the 1:2 adduct formed initially, which reacted slowly with residual PtCl<sub>2</sub> yielding a yellow solid, which was filtered, washed with CH<sub>2</sub>Cl<sub>2</sub> and *n*-pentane and dried under reduced pressure. Yield, 85%. Anal. Calc. (%) for C<sub>6</sub>H<sub>11</sub>Cl<sub>2</sub>NPtS<sub>2</sub> (427.07): C, 16.87; H, 2.60; N, 3.28; S, 14.99. Found: C, 16.70; H, 2.52; N, 3.39; S, 14.72. IR data: 1583 (v, N-CSS); 325, 313 (v, Pt-Cl) cm<sup>-1</sup>.

[PtCl(PyDT)]<sub>5</sub> (**2**) has been prepared by thermal degradation of **1** (following the thermogravimetric profile). A solid sample of **1** (400 mg) was heated gradually in oil bath up to 200 °C under reduced pressure, and maintained at this temperature for 5 hours. The complexes are slightly soluble in dichloroethane, from which they precipitate as orange aggregates by addition of *n*-pentane. Yield, 92%. Anal. Calc. (%) for 5×(C<sub>5</sub>H<sub>8</sub>ClNPtS<sub>2</sub>) 5×(376.58): C, 15.95; H, 2.15; N, 3.72; S, 16.99. Found: C, 15.78; H, 2.05; N, 3.90; S, 17.20. IR data: 1551 (v, N-CSS); 317 (v, Pt-Cl) cm<sup>-1</sup>.

[PtCl(PyDT)(PPh<sub>3</sub>)]·0.5CH<sub>2</sub>Cl<sub>2</sub> (**3**): 0.31 mmol of PPh<sub>3</sub> and 0.31 mmol of **2** were suspended in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. After 30 min a limpid red/orange solution was obtained. Suitable crystals for X-ray diffraction were obtained by slow addition of *n*-pentane (10 mL). Yield, 71%. Anal. Calc. (%) for C<sub>22.5</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>2</sub>PPtS<sub>2</sub> (669.38): C, 40.37; H, 3.62; N, 2.09; S, 9.56. Found: C, 40.48; H, 3.75; N, 2.15; S, 9.90. IR data: 1520 (v, N-CSS); 292 (v, Pt-Cl) cm<sup>-1</sup>.

[PtCl(PyDT)(DMSO)] (**4**) was prepared by addition of **5** (0.7 mmol) to a dimethyl sulfoxide solution in dichloromethane (3.8 mmol in 5 mL). The resulting yellow solution contained a small residue, which was discarded. On standing overnight the separated solution, a yellow powder was obtained, filtered, washed with abundant diethyl ether, and dried under reduced pressure. Yield, 70 %. Anal. Calc. (%) for C<sub>7</sub>H<sub>14</sub>ClNOPtS<sub>3</sub>: C, 18.49; H, 3.11; N, 3.08; S, 21.11. Found: C, 18.62; H, 3.22; N, 3.28; S, 21.52. IR data: 1559 (v, N-CSS); 314 (v, Pt-Cl) cm<sup>-1</sup>.

**Table S1.** Thermogravimetric (TG) and Differential Thermal Analysis (DTA) Data.

Complex	Decomposition (°C) Step	% weigh loss		DTA peak temp, °C (process <sup>a</sup> )
		found	calcd	
<b>1</b>	150-214 (– CH <sub>3</sub> Cl)	12.3	11.8	180 endo, 209 endo
	214-400 to Pt	41.6	42.5	338 exo, 368 exo
<b>2</b>	210-410 to Pt	47.7	48.2	340 exo, 370 exo
<b>3</b>	174-193 (– 0.5 CH <sub>2</sub> Cl <sub>2</sub> )	6.8	6.3	187 endo, 214 endo
	288-624 to Pt	59.2	62.9	367 exo, 453 exo
<b>4</b>	125-275 (– DMSO)	30.8	30.2	169 endo
	280-400 to Pt	47.7	48.5	391 exo

<sup>a</sup> endo, exo; endothermic/exothermic process

#### X-Ray Crystallographic Studies:

Crystals of **2** and **3** were lodged in Lindemann glass capillaries and centered on a four circle Philips PW1100 diffractometer using graphite monochromated MoK $\alpha$  radiation (0.71073Å), following the standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The diffraction data were corrected for Lorentz-Polarization effects and for absorption, as described by North et al.<sup>S2</sup> The structures were solved by standard direct methods and subsequently completed by Fourier syntheses.<sup>S3</sup> Non-hydrogen atoms were refined anisotropically in all the structures. Hydrogen atoms, were introduced at the calculated positions with fixed isotropic thermal parameters (1.2 U<sub>equiv</sub> of the parent carbon atom). Structure refinement and final geometrical calculations were carried out with the SHELXL-97 and WinGX programs.<sup>S4</sup>

**Table S2.** Selected bond distances (Å) and angles (°) for complex **3**.

Pt1–P1	2.2559(16)	P1–Pt1–S17	97.67(7)
Pt1–S17	2.293(2)	P1–Pt1–Cl1	94.54(7)
Pt1–S18	2.334(2)	S17–Pt1–S18	75.33(7)
Pt1–Cl1	2.3614(17)	Cl1–Pt1–S18	92.18(7)
P1–C21	1.827(6)	P1–Pt1–S18	172.25(6)
P1–C31	1.837(6)	S17–Pt1–Cl1	166.84(7)
P1–C41	1.812(6)	C16–S17–Pt1	87.6(2)
N11–C12	1.467(9)	C16–S18–Pt1	85.9(2)
N11–C15	1.477(8)		
N11–C16	1.306(8)		
C16–S17	1.738(7)		
C16–S18	1.716(7)		

## REFERENCES

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