

Supplementary Information

A Highly Water-Soluble Platinum(II) Complex Containing a Thiopropyl-1,2-dicarba-*closo*-dodecaborane(12) Ligand Functionalised with a Pendant Glycerol Group

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Experimental

All reactions were carried out at atmospheric pressure under nitrogen, unless otherwise stated and manipulations were performed using conventional Schlenk techniques. Tetrahydrofuran (THF) was pre-dried over sodium wire and distilled from benzophenone. Benzene, toluene and diethyl ether were distilled from sodium wire. Dichloromethane was distilled from CaH_2 . Acetonitrile was dried over calcium hydride and stored over 4Å molecular sieves. Distilled water was used in all experiments. All reagents were obtained commercially and used as received without further purification, except for AlCl_3 which was purified by vacuum sublimation and stored under nitrogen prior to use.

Thin Layer Chromatography (TLC) was carried out on aluminium backed silica plates (Merck Kieselgel 60 F254). Flash column chromatography was performed using silica gel (Merck Kieselgel 60) with solvents as indicated.

^1H (300.13 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz) spectra were recorded on a Bruker Avance DPX300 spectrometer at 300 K. Spectra were referenced either to TMS or to residual solvent resonances as an internal reference. $^{11}\text{B}\{^1\text{H}\}$ NMR (128.40 MHz) and $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.69 MHz) spectra were recorded on a Bruker Avance DPX400 spectrometer. Spectra were referenced to the external standards $\text{BF}_3\cdot\text{Et}_2\text{O}$ (δ 0.00) and 0.1 M $\text{Na}_2[\text{PtCl}_6]$ in D_2O (δ 0.00), respectively. All NMR spectra were recorded in ppm.

Low resolution mass spectra (ESI-MS) were obtained on a Finnegan LCQ MS Detector equipped with Finnegan LCQ data processing software using HPLC grade

MeOH. Elemental analyses were performed by the Chemical and MicroAnalytical Services (CMAS), Victoria (Australia).

2-[2(3-bromopropyl)-1,2-dodecaborane-1-ylmethoxyl]-1,3-dibenzyloxypropane (**2**) and [Pt(MeCN)(terpy)](OTf)₂ were prepared by the methods of Sjöberg *et al.*¹¹ and Büchner *et al.*,¹⁶ respectively.

2-[2(3-benzythiolpropyl)-1,2-dodecaborane-1-ylmethoxyl]-1,3-

dibenzyloxypropane (3). Benzyl mercaptan (0.40 mL, 2.90 mmol) was added to a solution of NaOEt (prepared by dissolving Na (65.0 mg, 2.80 mmol) in EtOH (15 mL)) and the solution was stirred for 1 h. A solution of **2** (0.50 g, 0.91 mmol) in EtOH (5 mL) was then added, and the mixture was stirred overnight. The mixture was poured into H₂O (15 mL) and the aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried over Na₂SO₄. The solution was concentrated *in vacuo* to give **3** as a colourless oil (0.44 g, 81 %) which was used without further purification. High-resolution (accurate mass) EI-MS: Calcd *m/z* 593.41067, Found *m/z* 593.41152 ([M+H]⁺); ESI-MS (MeOH + Ag⁺ ions) *m/z* 700.4 ([M+Ag]⁺); δ_H (300.13 MHz, CDCl₃) 7.22-7.33 (m, 15 H, aromatic), 4.48 (s, 4 H, PhCH₂O), 4.16 (s, 2 H, OCH₂C_{cage}), 3.83 (s, 2 H, SCH₂Ph), 3.75 (m, 1 H, CH₂CHCH₂), 3.52-3.62 (m, 4 H, CH₂CHCH₂), 3.38 (m, 2 H, CH₂CH₂S), 2.21 (m, 2 H, C_{cage}CH₂CH₂), 1.75 (m, 2 H, CH₂CH₂CH₂); δ_C (300.13 MHz, CDCl₃) 129.4-127.0 (aromatic), 79.3 (CH₂CHCH₂), 78.6 (C_{cage}), 77.2 (C_{cage}), 73.5 (PhCH₂O), 70.7 (OCH₂C_{cage}), 70.6 (CH₂CHCH₂), 36.2 (SCH₂Ph), 33.6 (C_{cage}CH₂CH₂), 30.4 (CH₂CH₂S), 29.0 (CH₂CH₂CH₂); δ_B (128.40 MHz, CDCl₃) -4.1 (2B), -11 (8B).

2-[2(3-thiolpropyl)-1,2-decaborane-1-ylmethoxyl]-1,3-dibenzyloxypropane (4).

AlCl₃ (330 mg, 2.50 mmol) in benzene (25 mL) was stirred at 50 °C for 30 min. After the addition of **3** (177 mg, 0.30 mmol), the mixture was stirred at 50 °C for a further 24 h. Benzene was removed *in vacuo* and the residue was re-dissolved in CH₂Cl₂ (30 mL). A solution of potassium sodium(+)-tartrate (1 M, 50 mL) was added and the mixture was stirred for 30 min. The organic layer was separated, filtered and dried over Na₂SO₄. The solvent was then removed *in vacuo* to give a colourless oil. Hexane was added to dissolve the diphenylmethane by-product and decanted after trituration. The crude product was recrystallised from MeOH to give **4** as an off-white gelatinous solid (32.7 mg, 34 %). ESI-MS (MeOH): *m/z* 320 ([M-H]⁻); δ_H (300.13 MHz, CDCl₃) 4.20 (s, 2H, OCH₂C_{cage}), 3.73 (m, 4 H, CH₂CHCH₂), 3.56 (m, 1 H, CH₂CHCH₂), 2.53 (m, 2 H, CH₂CH₂S), 2.35 (m, 2 H, C_{cage}CH₂CH₂), 1.75 (m, 2 H, CH₂CH₂CH₂), 1.63 (s, 2 H, OH), 1.43 (t, *J* = 8 Hz, 1 H, SH); δ_C (300.13 MHz, CDCl₃) 81.3 (CH₂CHCH₂), 78.2 (C_{cage}), 77.2 (C_{cage}), 70.1 (OCH₂C_{cage}), 62.7 (CH₂CHCH₂), 33.3 (C_{cage}CH₂CH₂), 33.1 (CH₂CH₂CH₂), 24.0 (CH₂CH₂S); δ_B (128.40 MHz, CDCl₃) -3.9 (2B), -10.9 (8B).

2-[2(3-propanethiolato)-1,2-carborane-1-ylmethoxyl]-1,3-propanediol-2,2':6',2''-terpyridineplatinum(II) triflate (5). To a solution of **4** (34.5 mg, 0.11 mmol) in acetone (5 mL) was added [Pt(MeCN)(terpy)](OTf)₂ (82.1 mg, 0.11 mmol). The solution turned immediately orange-red and stirring was continued for 3 h at room temperature. Diethyl ether was then added to precipitate out **5** as an orange, microcrystalline solid (36.4 mg, 46 %) which was found to be hygroscopic in air. (Found: C, 32.57; H, 4.53; N, 3.94%. C₂₅H₃₆O₆B₁₀F₃N₃PtS₂·1.5H₂O requires C,

32.41; H, 4.24; N, 4.54%). ESI-MS (MeOH): m/z 749.3 (M^+); δ_H (300.13 MHz, d_6 -acetone) 9.77 (d, $^3J_{HH} = 2.7$ Hz, $^3J_{PtH} = 38$ Hz, H2), 8.71 (m, H5, H8, H9), 8.51 (t, $^3J_{HH} = 7.8$ Hz, H4), 7.93 (t, $^3J_{HH} = 6.1$ Hz, H3), 4.15 (s, 2H, OCH_2C_{cage}), 3.60 (m, 2 H, CH_2CH_2S), 3.32 (m, 4 H, CH_2CHCH_2), 3.2 (m, 1 H CH_2CHCH_2), 2.57 (m, 2 H, $C_{cage}CH_2$), 2.33 (m, 2 H, $CH_2CH_2CH_2$); δ_C (300.13 MHz, d_6 -acetone) 160.6, 155.8, 154.5, 144.8, 131.1, 127.5, 126.0 (terpy), 101.0 (CH_2CHCH_2), 79.8 (C_{cage}), 79.0 (C_{cage}), 69.3 (OCH_2C_{cage}), 62.68 (CH_2CHCH_2), 34.3 ($C_{cage}CH_2CH_2$), 31.5 ($CH_2CH_2CH_2$), 27.4 (CH_2CH_2S); δ_B (128.40 MHz, $CDCl_3$) -4.4 (2B), -11.2 (8B); δ_{Pt} (85.69 MHz, d_6 -acetone) -3072.