Electronic Supplementary Material (ESI) for Dalton Transactions.

Bis(dimethylsulfoxide)carbonateplatinum(II), a new synthon for a low-impact, versatile synthetic route to anticancer Pt carboxylates.

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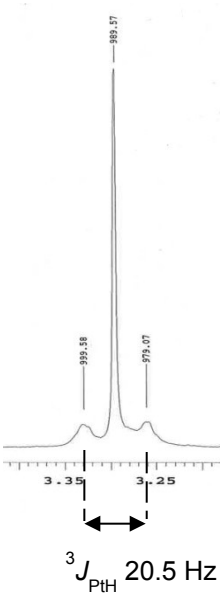

Fig. S1 - ^{1}H NMR signal of S-coordinated DMSO in complex **1** in D_2O (300 MHz)

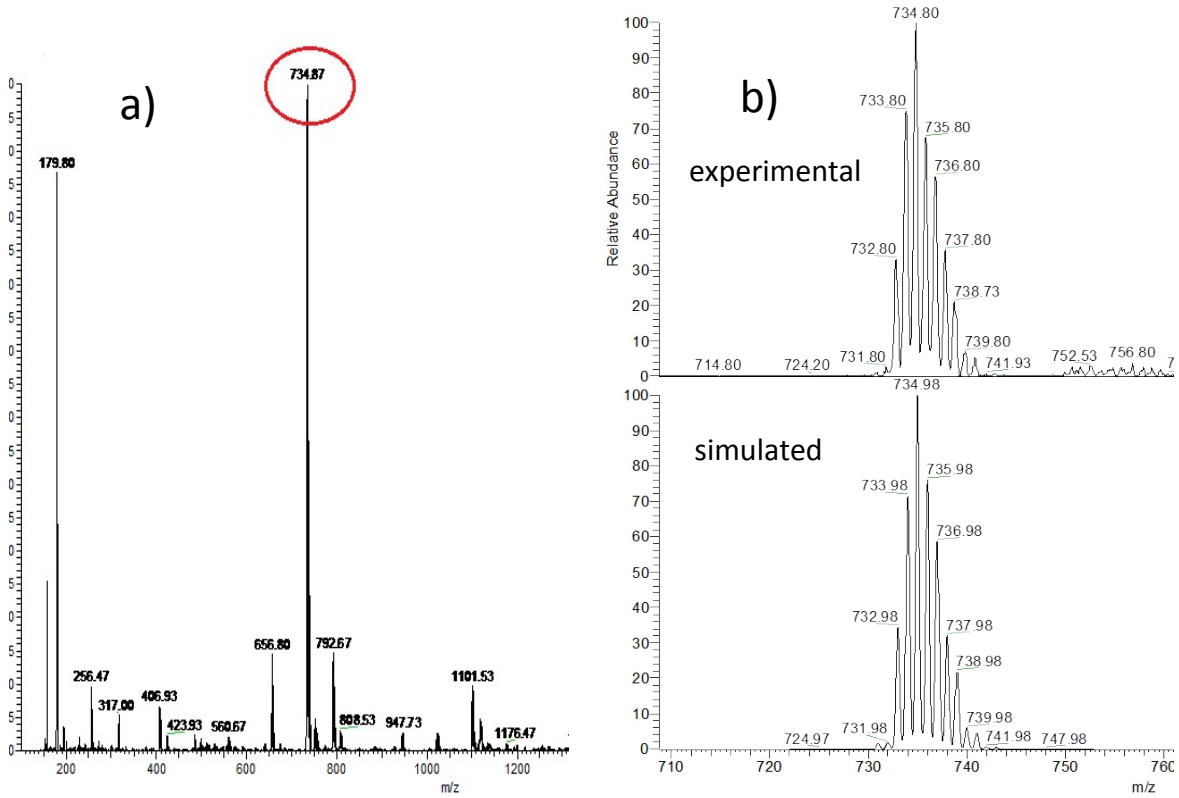

Fig. S2 – a) MS-ESI spectrum of **1;** b) experimental and simulated signal of $[(Me_2SO\text{-}S)_4Pt_2\mu(O)\mu(OH)]^+$.

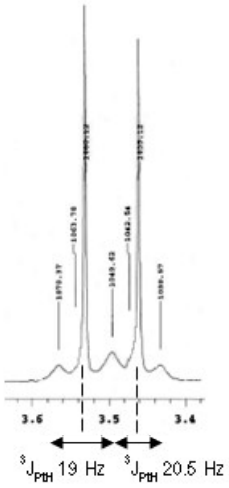

Fig. S3 – Overlapped ^{1}H-NMR signals of coordinated inequivalent DMSO in complex **4** (acetone-d_6, 300 MHz)

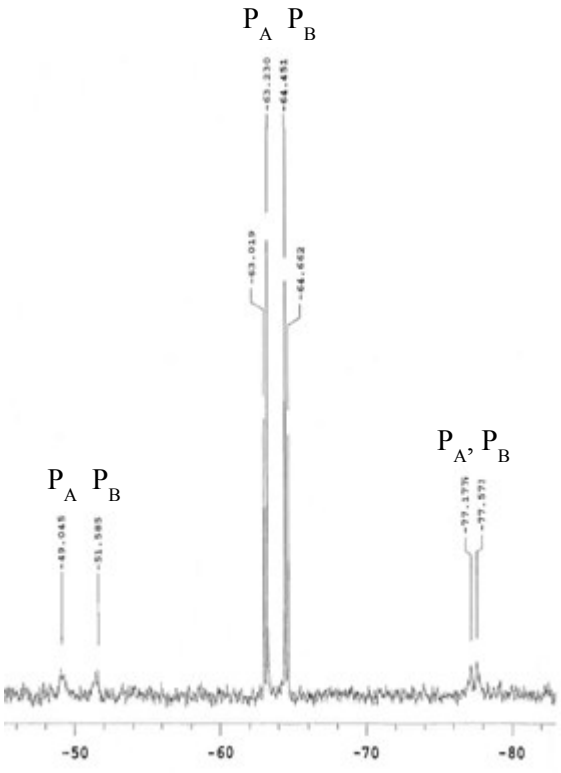

Fig. S4 – ^{31}P NMR of complex **7** in DMSO (121.50 MHz)

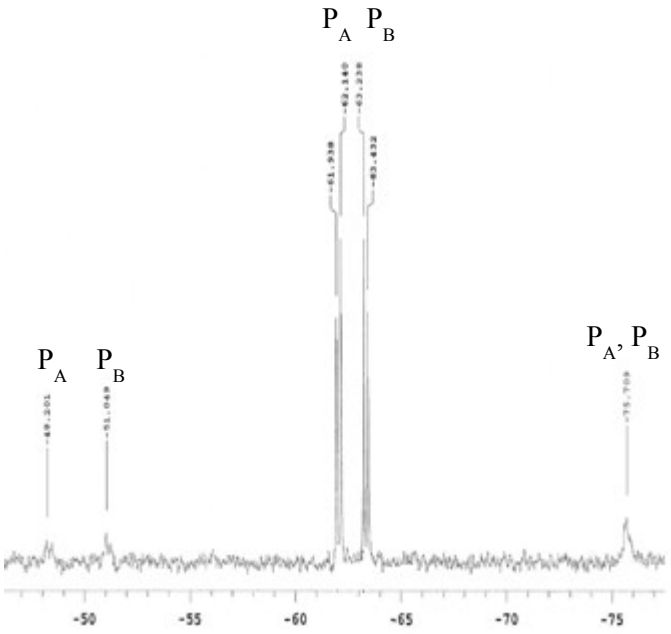

Fig. S5 **–** ^{31}P NMR of complex **8** in DMSO (121.50 MHz).

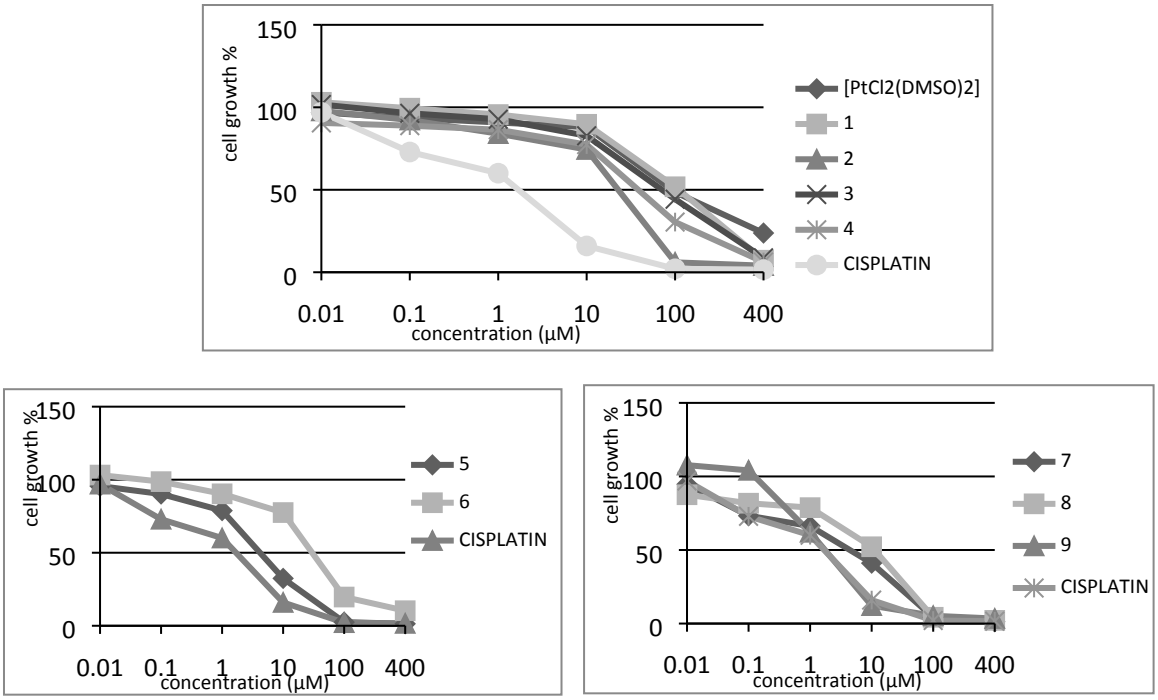

Fig. S6 **–** Inhibitory effects on cell proliferation of A2780 cell line.

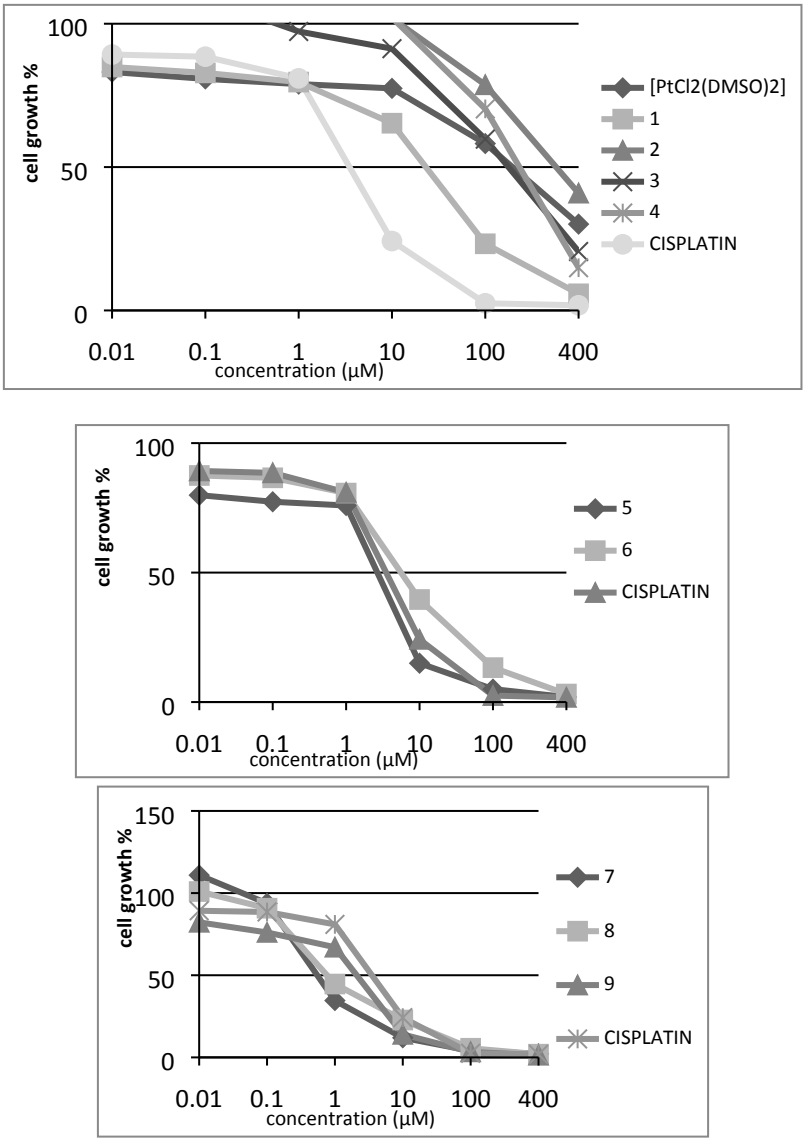

Fig. S7 **–** Inhibitory effects on cell proliferation of SKOV-3 line.

New synthesis of known compounds: carbonate substitution with O-donor ligands. Characterization of the products.

A) Reaction of 1 with cyclohexanedicarboxylic acid (CBDC): a new way to [Pt(CBDC)(Me_2SO-*S*)$_2$] (A) (ref 16)

Complex [$PtCO_3$(Me_2SO-*S*)$_2$] (50 mg, $1.2\cdot 10^{-4}$ mol, MW 411.2 g/mol), solubilized in 5 mL of H_2O, was put under vigorous stirring at room temperature. CBDC (17 mg, $1.2 \cdot 10^{-4}$ mol, MW 144.1 g/mol, 1 eq), solubilized in H_2O, was added dropwise. The solution was left for 20 hours under vigorous stirring. The solution was then taken to dryness leaving [Pt(CBDC)(Me_2SO-*S*)$_2$] as a cream solid (42 mg, $8.5 \cdot 10^{-5}$ mol, MW 493.2 g/mol, yield 71%), soluble in H_2O and DMSO. ^{1}H NMR (D_2O): δ = 1.8 (m, 2H, CH_2), 2.64 (m, 4H, CH_2), 3.4 (s, 6H, DMSO) ppm.^{13}C NMR (D_2O): δ = 16.13 and 31.52 (3 CH_2 of CBDA), 42.80 (CH_3 of DMSO), 56.53 (C) , 180.22 (COO).

B) Reaction of 1 with malonic acid: a new way to [Pt(malonate)(Me_2SO-*S*)$_2$] (B).

Complex [$PtCO_3$(Me_2SO-*S*)$_2$] (50 mg, $1.22 \cdot 10^{-4}$ mol, MW 411.2 g/mol), solubilized in 10 mL of CH_3OH, was put under vigorous stirring. Malonic acid (13 mg, $1.22 \cdot 10^{-4}$ mol, MW 104.1 g/mol, 1eq), solubilized in 5 mL of CH_3OH, was added to the first solution. No change of color or precipitate was observed. The solution was left for 2 hours under the stirring, then it was taken to dryness by rotary evaporator and the solid residue was dried under vacuum over P_2O_5 for one night. Complex **B** was obtained as a white solid (40 mg, $8.83 \cdot 10^{-5}$ mol, MW 453.16 g/mol, 72%).^{1}H NMR (CD_3OD): δ = 2.63 (s, 2H, CH_2), 3.46 (s, $^3J_{PtH}$ 20.5 Hz, 12 H, DMSO) ppm.^{13}C NMR (CD_3OD): δ = 40.39 (s, CH_2), 42.72 (s, CH_3, DMSO), 175.85 (s, COO) ppm.^{195}Pt NMR: δ = -3193 ppm

Exchange of DMSO for PPh_3 to give [Pt(malonate)(PPh_3)$_2$](NMR experiment in DMSO):

^{31}P NMR (DMSO-d_6): δ = 9.47 (s, $^1J_{PtP}$ 3910 Hz, PPh_3) ppm.

C) Reaction of 1 with oxalic acid: a new way to [Pt(oxalate)(Me_2SO-*S*)$_2$] (C).

Complex **C** was prepared in the same condition as complex **B**, using oxalic acid (15 mg, $1.22 \cdot 10^{-4}$ mol, MW 126.1 g/mol, 1 eq). A white precipitate was immediately observed. The mixture was kept under stirring for 10 min and then filtered. The white solid product [Pt(oxalate)(Me_2SO-*S*)$_2$], **C**, was dried under vacuum (48 mg, $1.09 \cdot 10^{-4}$ mol, MW 439.5 g/mol, yield 89%). ^{1}H NMR (DMSO-d_6): δ = 3.5 (s, 12H, $^3J_{HPt}$ not resolved, DMSO) ppm.

Exchange of DMSO for PPh_3 to give [Pt(oxalate)(PPh_3)$_2$](NMR experiment in DMSO or $CDCl_3$):

^{31}P NMR (DMSO-d_6): δ = 7.51 (s, $^1J_{PtP}$ 3766 Hz) ppm.^{31}P NMR ($CDCl_3$): δ = 7.73 (s, $^1J_{PtP}$ 3780 Hz) ppm.

D) Reaction of 1 with *L*-carnitine to give [Pt(*L*-carnitine)(Me_2SO-*S*)$_2$]BF_4 (D)

The synthesis and characterization of complex **D** has been described in ref 9.

$C_{11}H_{26}BF_4NO_5PtS_2$ (598)**:** % found (% calc. for) C 21.90 (22.10), H 4.45 (4.38) and N 2.30 (2.34).

^{1}H NMR (300 MHz D_2O, 25°C) δ = 2.2 (bm, 2H, CH_2COO), 3.1 (s, 9H, Me_3N^+), 3.2 (m, 2H, CH_2N), 3.5 (s, 12 H, CH_3 DMSO), 4.2 (m, 1H, CHO) ppm. ^{1}H NMR (300 MHz d_6-DMSO, 25°C) δ = 2.2 (bm, 2H, CH_2COO), 3.1 (s, 9H, Me_3N^+), 3.3 (m, 12 H, CH_3 of DMSO + 2H, CH_2N), 4.2 (m, 1H, CHO) ppm. ^{195}Pt NMR (85.64 MHz, DMSO, 25°C) δ = -3193.5 ppm. MS-ESI: observed m/z 511, calculated 511.4 for $C_{11}H_{26}NO_5PtS_2$ (M^+).

Table S1. Experimental details for **X-Ray Crystallography**

	Complex **3**	Complex **4**	Complex **6**
Crystal data			
Chemical formula	$C_{11}H_{22}O_8PtS_2$	$C_{11}H_{16}O_5PtS_2$	$C_{43}H_{34}O_3P_2Pt$
M_r	541.49	487.44	855.73
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$	Triclinic, P-1
a, b, c (Å)	9.4289 (2), 10.5381 (2), 16.9406 (3)	14.6904(2), 19.7530(4), 10.1449(4)	11.2726 (2), 12.5875 (3), 14.9124 (3)
α , β , γ (°)	90, 90, 90	90, 95.117(1), 90	107.454 (1), 99.969 (1), 103.422 (1)
V (Å^3)	1683.26 (6)	2932.1(1)	1895.05 (7)
Z	4	8	2
μ (mm^{-1})	8.62	9.86	3.82
Crystal size (mm)	0.29 × 0.28 × 0.23	0.29 x 0.21 x 0.10	0.29 x 0.16 x 0.09
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15456, 4014, 3950	15507, 5659, 5137	29500, 9155, 7811
R_{int}	0.064	0.066	0.059
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.099, 1.11	0.065, 0.188, 1.03	0.038, 0.099, 1.06
No. of reflections	4014	5659	9155
No. of parameters	206	343	442
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.47, -3.10	2.70, -3.70	1.00, -2.50

Table S2. Selected Bond Distances and Angles and Geometrical Parameters for Intermolecular Interactions in **3** (Å, deg)

Bond distances		Bond angles	
Pt1 - S1	2.224(3)	S1 - Pt1 - S2	93.44(1)
Pt1 - S2	2.216(3)	S1 - Pt1 - O3	92.04(2)
Pt1 - O3	2.016(7)	S2 - Pt1 - O5	90.90(2)
Pt1 - O5	1.984(8)	O3 - Pt1 - O5	83.46(3)

Intermolecular interactions

	D-H	D....A	H....A	D-H...A
O6-H...O5	0.88(13)	2.63(1)	1.89(20)	139(11)
C2-H...O2	0.96	3.07(2)	2.30	137
O7-H...O6^{i}	0.82	2.74(1)	1.95	160
C1-H...O7^{ii}	0.96	3.31(2)	2.41	155
C2-H...O1^{iii}	0.96	3.22(1)	2.31	157
C4-H...O8^{iv}	0.96	3.24(2)	2.31	160
O8-H...O1^{v}	0.88(13)	2.93(1)	2.10(18)	156(10)

Symmetry code: (i) 2-x,y+1/2,1/2-z; (ii) 3/2-x,-y,z+1/2; (ii) x+1/2,-y-1/2,1-z; (iv) 1-x,y-1/2,1/2-z; (v) x+1/2,1/2-y,1-z

Table S3. Selected Bond Distances and Angles and Geometrical Parameters for Intermolecular Interactions in **4** (Å, deg)

Bond distances		Bond angles	
Pt1 - S1	2.221(2)	S1 - Pt1 - S2	91.89(8)
Pt1 - S2	2.221(2)	S1 - Pt1 - O1	86.9(2)
Pt1 - O1	2.010(7)	S4 - Pt2 - O6	87.9(2)
Pt1 - O3	1.992(7)	S2 - Pt1 - O3	89.7(2)
Pt2 - S3	2.219(3)	S3 - Pt2 - S4	92.0(1)
Pt2 - S4	2.225(3)	S3 - Pt2 - O8	88.0(2)
Pt2 - O6	1.996(7)	O6 - Pt2 - O8	92.4(3)
Pt2 - O8	2.004(7)	O1 - Pt1 - O3	91.5(3)

Intermolecular interactions

	D-H	D....A	H....A	D-H...A
C8-H...O7	0.96	3.19(1)	2.37	143
C9-H...O7	0.96	3.15(1)	2.37	138
C8-H...O5^{i}	0.96	3.21(1)	2.38	144
C9-H...O4^{ii}	0.96	3.28(1)	2.45	144
C11-H...O2^{iii}	0.96	3.34(2)	2.49	147
C10-H...O2^{iii}	0.96	3.41(1)	2.63	138
C10-H...O9^{iv}	0.96	3.37(2)	2.50	152
C20-H...O2^{v}	0.96	3.36(2)	2.53	145
C19-H...O2^{v}	0.96	3.45(2)	2.57	154

Symmetry codes: (i) x,3/2-y,z+1/2; (ii) x,3/2-y,z-1/2; (iii) -x,y+1/2,3/2-z; (iv) x-1,3/2-y,z+1/2; (v)1-x,1-y,1-z

Table S4. Selected Bond Distances and Angles and Geometrical Parameters for Intermolecular Interactions in **6** (Å, deg)

Bond distances		Bond angles	
Pt1 - P1	2.253(1)	P1 - Pt1 - P2	100.12(5)
Pt1 - P2	2.255(1)	P2 - Pt1 - O1	83.18(1)
Pt1 - O1	2.047(4)	P1 - Pt1 - O3	87.02(1)
Pt1 - O3	2.013(5)	O1- Pt1 - O3	90.04/2)

Intermolecular interactions

	D-H	D....A	H....A	D-H...A
C9-H9...O2[i]	0.93	3.191(9)	2.44	138
C30-H30...O2[ii]	0.93	3.342(11)	2.60	137

Symmetry codes: (i) x-1,y,z; (ii) -x+1,-y,-z