Electronic Supplementary Information for Dalton Transactions

Hard/Soft ligand Selective Substitution Reactions in β-diketonate Platinum(II) Complexes

Sandra A. De Pascali,[a] Paride Papadia,[a] Serena Capoccia,[a] Luciano Marchiò,[b] Maurizio Lanfranchi,[b] Antonella Ciccarese[a], and Francesco P. Fanizzi*[a,c]

[a] *Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, prov.le Lecce/Monteroni, I-73100, Lecce, Italy. E-mail: fp.fanizzi@unile.it; Fax: +39 832 298 626; Tel: +39 832 298 867*
[b] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Parco Area delle Scienze 17A, 43100 Parma, Italy*
[c] *ConsortiumC.A.R.S.O.,CancerResearch Center, I-70100,Valenzano-Bari, Italy*

Electronic Supplementary Information

Table S1. Selected bond lengths (Å) and angles (deg) for **1a-1c**.

1a				**1b**		**1c**			
Pt(1)-Cl(1)	2.301(2)	Pt(2)-Cl(2)	2.293(3)	Pt-Cl	2.295(2)	Pt(1)-Cl(1)	2.272(2)	Pt(2)-Cl(2)	2.286(1)
Pt(1)-S(1)	2.201(2)	Pt(2)-S(2)	2.201(2)	Pt-S	2.254(2)	Pt(1)-P(1)	2.230(2)	Pt(2)-P(2)	2.232(2)
Pt(1)-O(1)	2.002(6)	Pt(2)-O(4)	2.012(6)	Pt-O(1)	1.999(4)	Pt(1)-O(11)	2.003(4)	Pt(2)-O(15)	2.008(3)
Pt(1)-O(2)	2.039(6)	Pt(2)-O(5)	2.024(6)	Pt-O(2)	2.033(4)	Pt(1)-O(21)	2.054(4)	Pt(2)-O(25)	2.057(3)
C(1)-O(1)	1.28(1)	C(8)-O(4)	1.27(1)	C(1)-O(1)	1.288(7)	C(11)-O(11)	1.284(6)	C(15)-O(15)	1.288(6)
C(1)-C(2)	1.39(1)	C(8)-C(9)	1.39(1)	C(1)-C(2)	1.407(9)	C(11)-C(21)	1.384(8)	C(15)-C(25)	1.375(8)
C(2)-C(3)	1.38(1)	C(9)-C(10)	1.37(1)	C(2)-C(3)	1.392(9)	C(21)-C(31)	1.382(8)	C(25)-C(35)	1.385(8)
C(3)-O(2)	1.29(1)	C(10)-O(5)	1.27(1)	C(3)-O(2)	1.267(7)	C(31)-O(21)	1.292(6)	C(35)-O(25)	1.282(6)
S(1)-O(3)	1.485(6)	S(2)-O(6)	1.471(6)	S-C(6)	1.789(7)				
S(1)-C(6)	1.759(9)	S(2)-C(13)	1.775(9)	S-C(7)	1.810(7)				
S(1)-C(7)	1.777(8)	S(2)-C(14)	1.770(10)						
S(1)-Pt(1)-Cl(1)	91.46(9)	S(2)-Pt(2)-Cl(2)	91.1(1)	S-Pt-Cl	88.81(7)	P(1)-Pt(1)-Cl(1)	95.20(6)	P(2)-Pt(2)-Cl(2)	92.08(5)
O(2)-Pt(1)-Cl(1)	86.3(2)	O(5)-Pt(2)-Cl(2)	86.8(2)	O(2)-Pt-Cl	88.6(1)	O(21)-Pt(1)-Cl(1)	85.8(1)	O(25)-Pt(2)-Cl(2)	86.5(1)
O(1)-Pt(1)-O(2)	93.8(2)	O(4)-Pt(2)-O(5)	92.8(2)	O(1)-Pt-O(2)	92.6(2)	O(11)-Pt(1)-P(1)	87.5(1)	O(15)-Pt(2)-P(2)	90.3(1)
O(1)-Pt(1)-S(1)	88.6(2)	O(4)-Pt(2)-S(2)	89.3(2)	O(1)-Pt-S	90.0(1)	O(11)-Pt(1)-O(21)	91.5(2)	O(15)-Pt(2)-O(25)	91.1(1)

Table S2. Selected bond lengths (Å) and angles (deg) for **2a-2c**.

2a		**2b**		**2c**			
Pt-S	2.200(2)	Pt-S	2.250(3)	Pt(1)-P(1)	2.218(2)	Pt(2)-P(2)	2.217(2)
Pt-O(3)	2.041(6)	Pt-O(3)	2.011(8)	Pt(1)-O(31)	2.048(4)	Pt(2)-O(32)	2.053(4)
Pt-O(4)	2.010(6)	Pt-O(4)	2.055(9)	Pt(1)-O(41)	2.067(4)	Pt(2)-O(42)	2.063(4)
Pt-C(2)	2.093(9)	Pt-C(2)	2.09(1)	Pt(1)-C(21)	2.064(6)	Pt(2)-C(22)	2.051(7)
C(1)-O(1)	1.23(1)	C(1)-O(1)	1.21(2)	C(11)-O(11)	1.213(8)	C(12)-O(12)	1.231(8)
C(1)-C(2)	1.46(1)	C(1)-C(2)	1.50(2)	C(11)-C(21)	1.494(8)	C(12)-C(22)	1.509(9)
C(2)-C(3)	1.48(1)	C(2)-C(3)	1.51(2)	C(21)-C(31)	1.480(8)	C(22)-C(32)	1.510(9)
C(3)-O(2)	1.22(1)	C(3)-O(2)	1.20(2)	C(31)-O(21)	1.226(7)	C(32)-O(22)	1.250(8)
C(6)-O(3)	1.28(1)	C(6)-O(3)	1.27(2)	C(61)-O(31)	1.259(7)	C(62)-O(32)	1.260(7)
C(6)-C(7)	1.38(1)	C(6)-C(7)	1.43(2)	C(61)-C(71)	1.376(9)	C(62)-C(72)	1.365(9)
C(7)-C(8)	1.40(1)	C(7)-C(8)	1.33(2)	C(71)-C(81)	1.392(9)	C(72)-C(82)	1.381(9)
C(8)-O(4)	1.29(1)	C(8)-O(4)	1.31(2)	C(81)-O(41)	1.267(7)	C(82)-O(42)	1.263(7)
S-C(11)	1.762(9)	S-C(11)	1.75(2)				
S-C(12)	1.763(9)	S-C(12)	1.75(2)				
S-O(5)	1.458(7)						
S-Pt-C(2)	89.8(3)	S-Pt-C(2)	95.0(3)	P(1)-Pt(1)-C(21)	93.6(2)	P(2)-Pt(2)-C(22)	92.7(2)
S-Pt-O(4)	90.9(2)	S-Pt-O(4)	88.8(2)	P(1)-Pt(1)-O(41)	88.4(1)	P(2)-Pt(2)-O(42)	89.5(1)
O(3)-Pt-O(4)	92.0(3)	O(3)-Pt-O(4)	92.3(3)	O(31)-Pt(1)-O(41)	90.7(2)	O(32)-Pt(2)-O(42)	90.2(2)
O(3)-Pt-C(2)	87.7(3)	O(3)-Pt-C(2)	84.0(4)	O(31)-Pt(1)-C(21)	87.3(2)	O(32)-Pt(2)-C(22)	87.6(2)

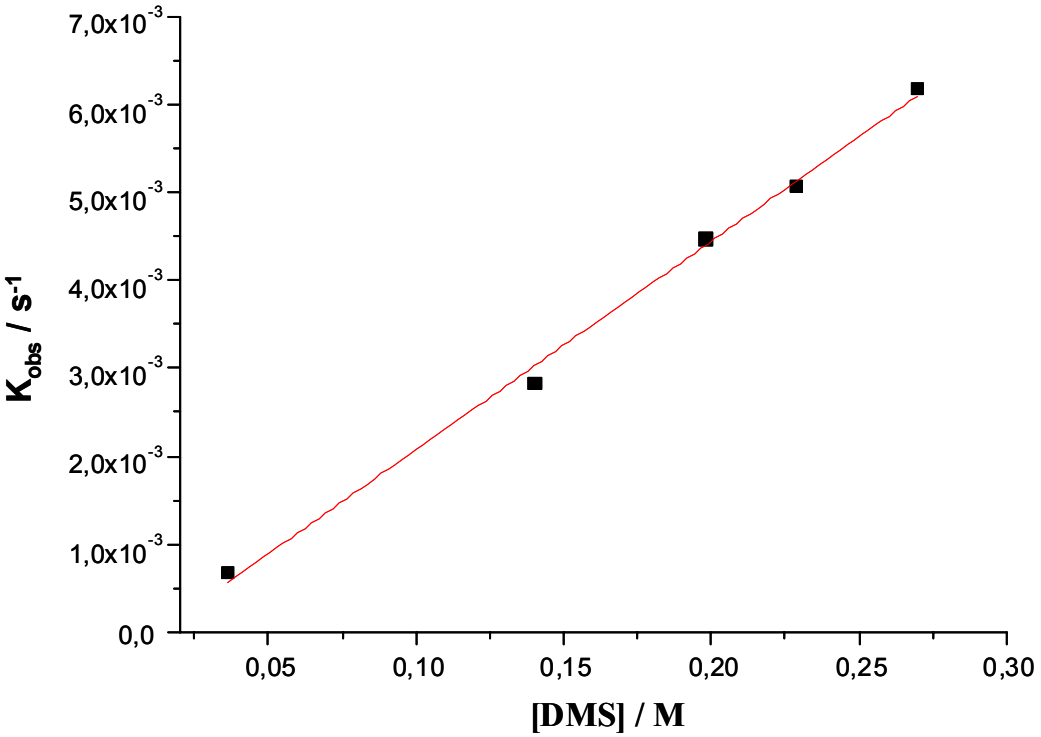

Figure S3. Pseudo-first-order rate constants k_{obs} as a function of [DMS] for reactions **1a→1b** at 283.15 K in $CDCl_3$.