Mixed valence Pt(II),Pt(IV),Pt(II) Complexes from a Diplatinum(III) Synthon and Sulfur Based Anions

Consuelo Fortuño* and Antonio Martín

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea-ISQCH, Universidad de Zaragoza-C.S.I.C., E-50009 Zaragoza, Spain.

E-mail: cfortuno@unizar.es

Piero Mastrorilli*, Stefano Todisco, Mario Latronico

DICATECh, Politecnico di Bari, I-70125 Bari, Italy

E-mail: p.mastrorilli@poliba.it

Summary of supporting information

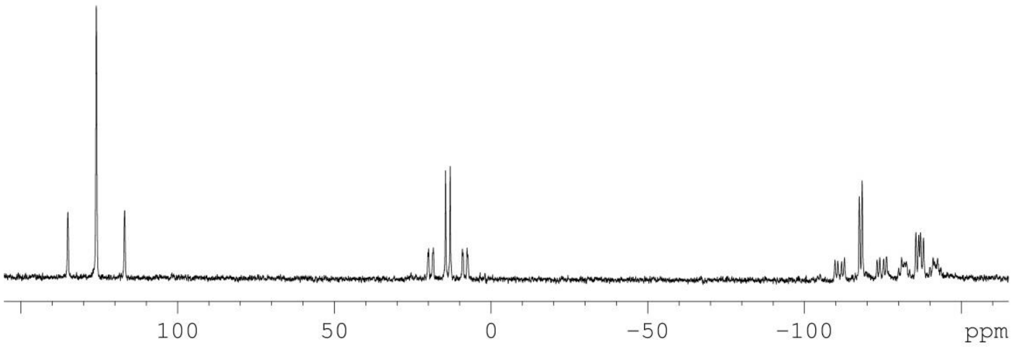

Figure S1 $^{31}P\{^{1}H\}$ NMR spectrum of **2a** (acetone-d_6, 298 K)

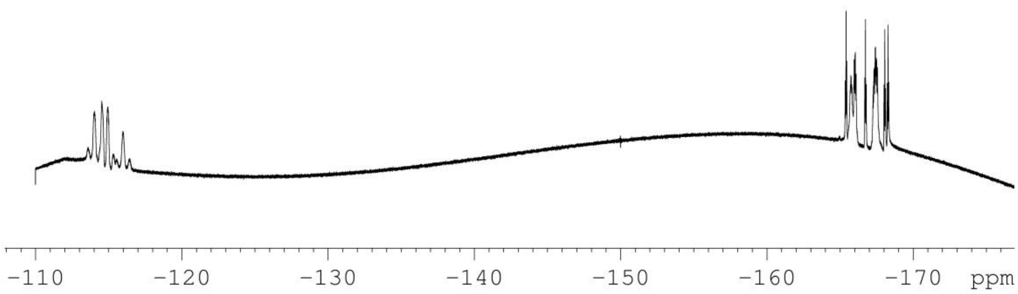

Figure S2 ^{19}F NMR spectrum of **2a** (acetone-d_6, 298 K)

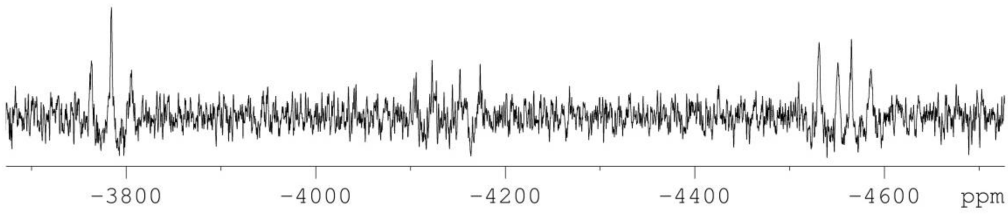

Figure S3 ^{195}Pt{^{19}F} NMR spectrum of **2a** (acetone-d_6, 298 K)

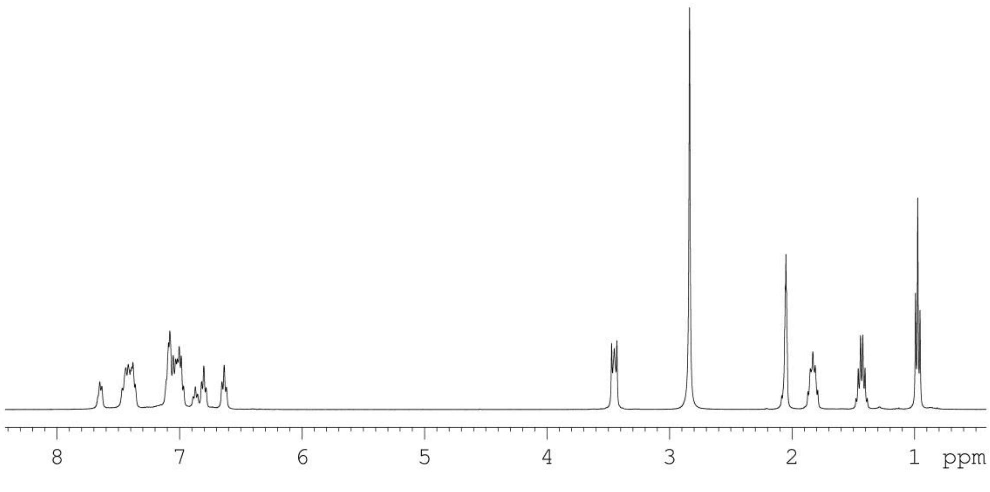

Figure S4 ^{1}H NMR spectrum of **2a** (acetone-d_6, 298 K)

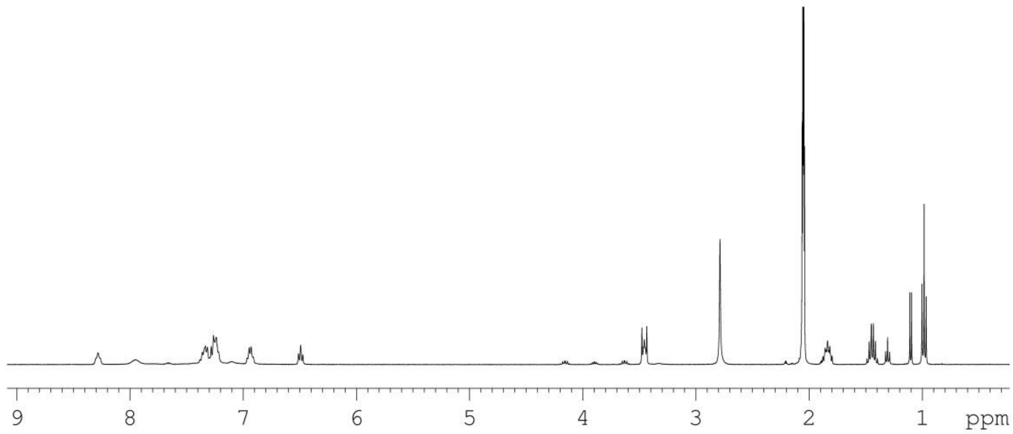

Figure S5 ^{1}H NMR spectrum of **3b** (acetone-d_6, 298 K)

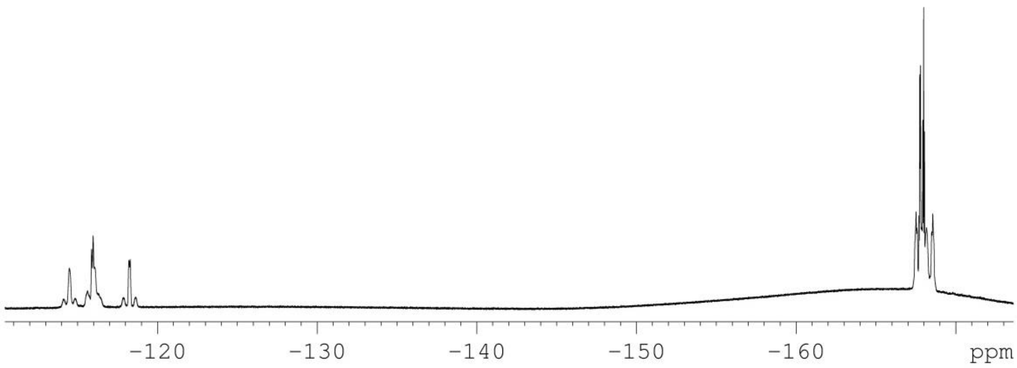

Figure S6 ^{19}F NMR spectrum of **3b** (acetone-d_6, 298 K)

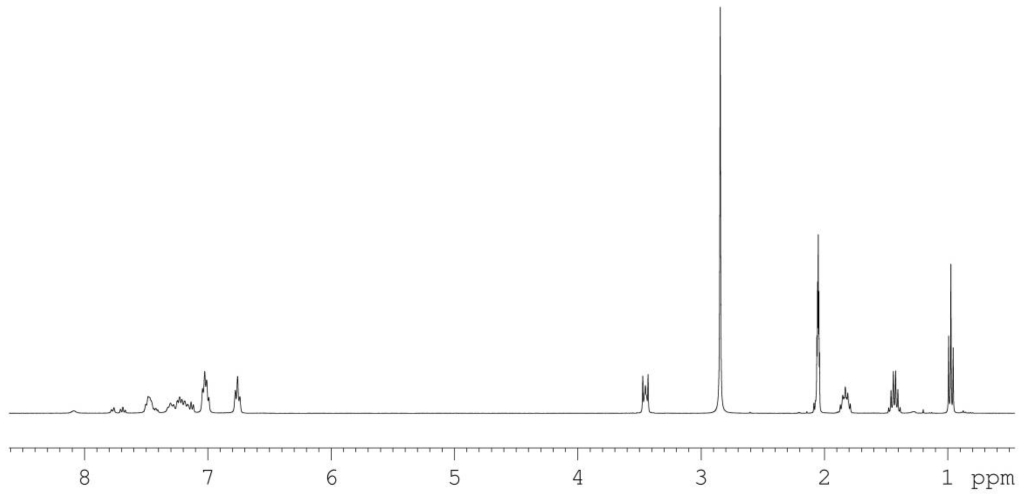

Figure S7 ^{1}H NMR spectrum of **2c** (acetone-d_6, 298 K)

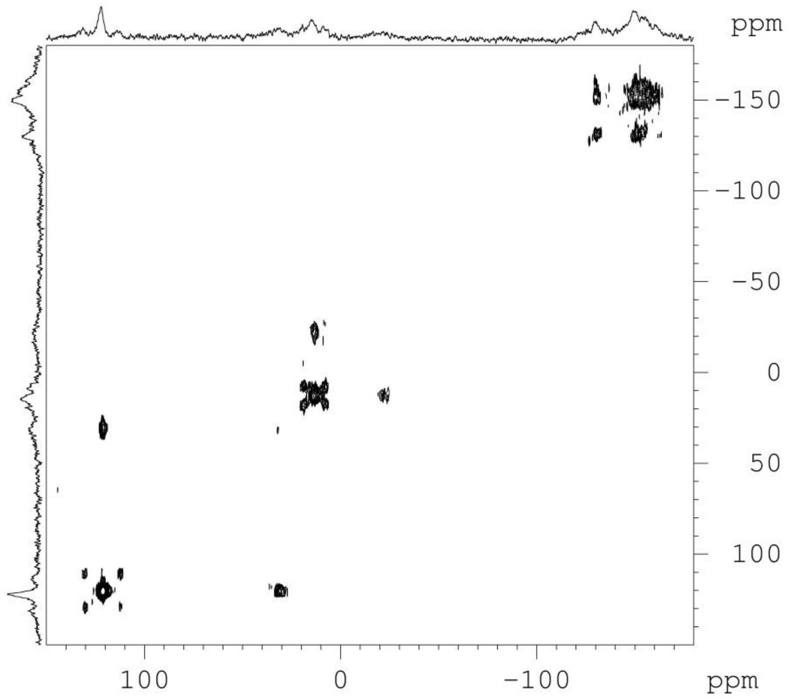

Figure S8. $^{31}P\{^{1}H\}$ EXSY spectrum of the solution obtained dissolving solid **4c** in deuteroacetone (τ_m = 0.050 s, T= 263 K).

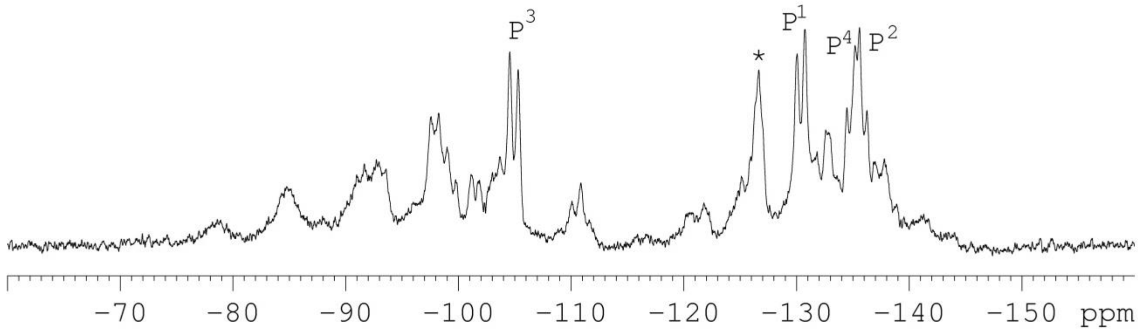

Figure S9. Portion of the low T $^{31}P\{^1H\}$ NMR spectrum of the solution obtained dissolving solid **3d** in acetone-d_6 (T = 223 K). The asterisked peak is due to residual **1**. Labels refer to **3d**.

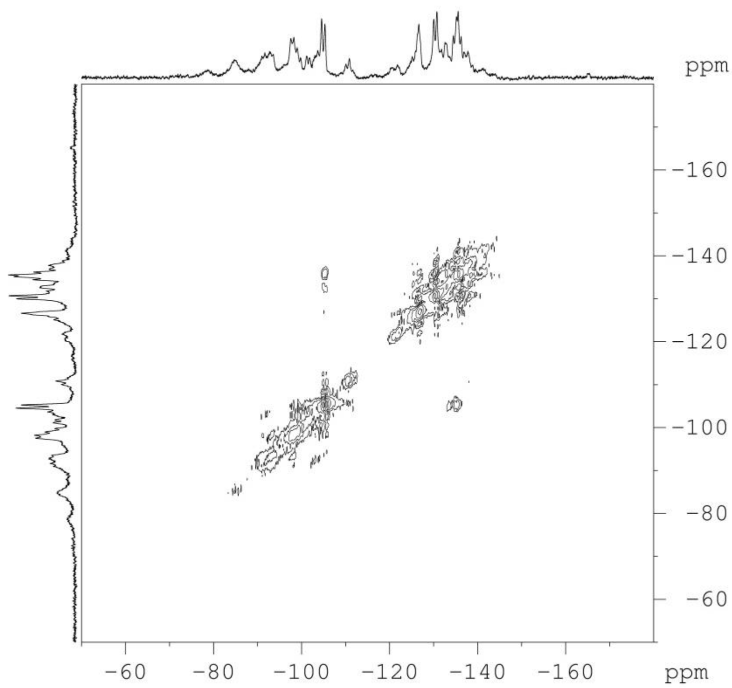

Figure S10. $^{31}P\{^1H\}$ COSY spectrum of the solution obtained dissolving **3d** in acetone-d_6 (T = 223 K)

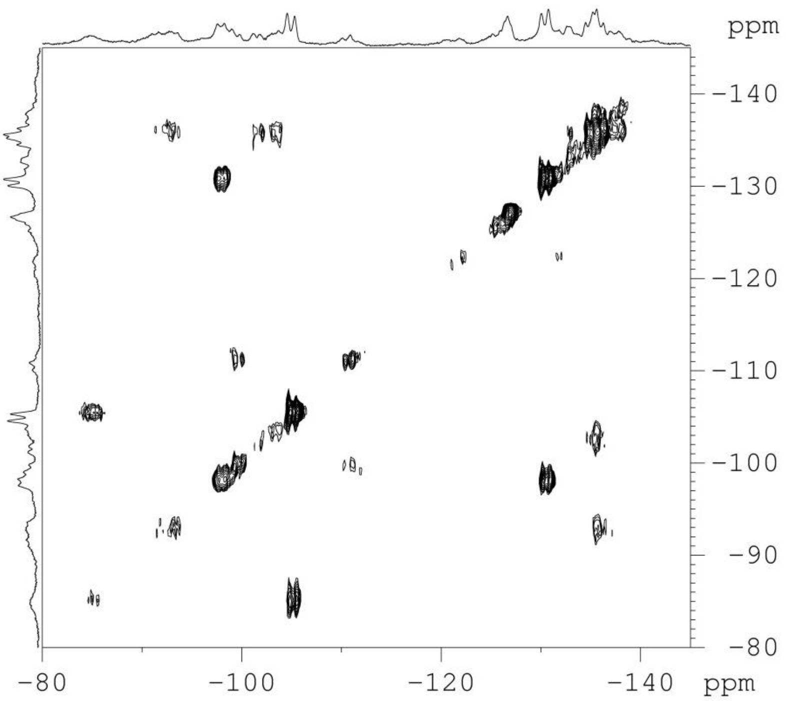

Figure S11. ${}^{31}P\{{}^{1}H\}$ EXSY spectrum of the solution obtained dissolving **3d** in acetone-*d*$_6$ (τ_m = 0.025 s, T = 223 K)

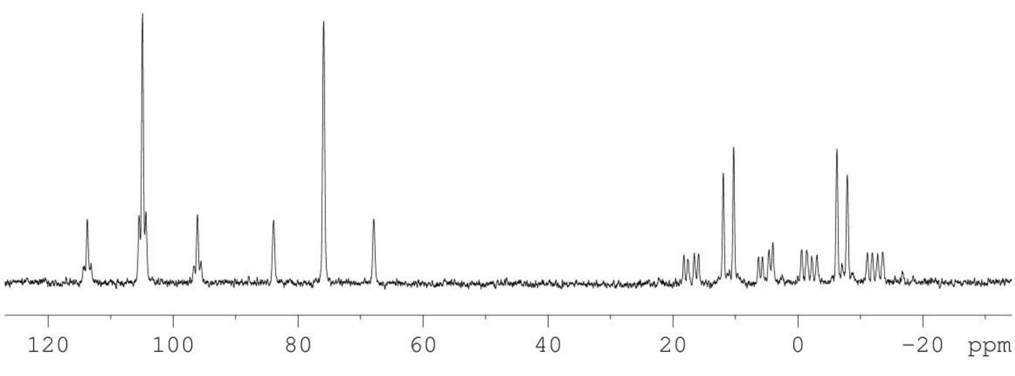

Figure S12 ${}^{31}P\{{}^{1}H\}$ NMR spectrum of **5d** (acetone-*d*$_6$, 298 K)

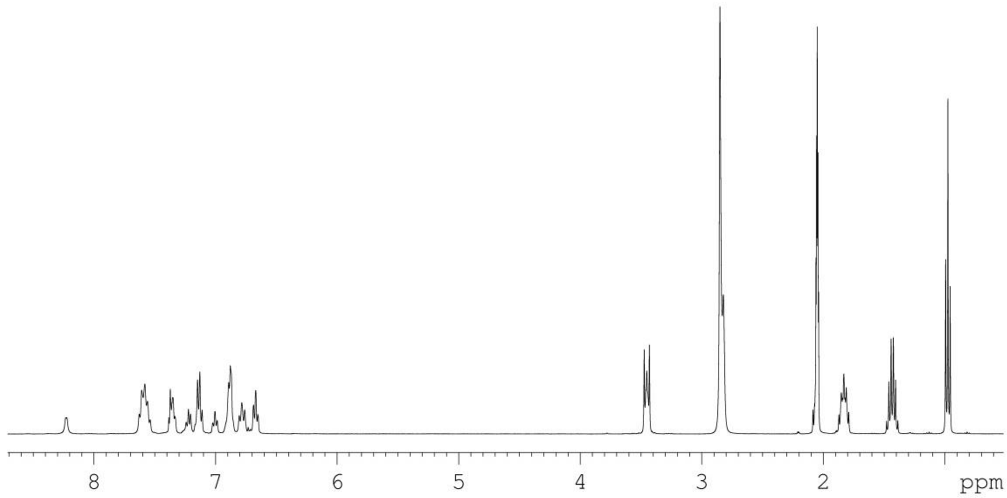

Figure S13 ^{1}H NMR spectrum of **2d** (acetone-d_6, 298 K)

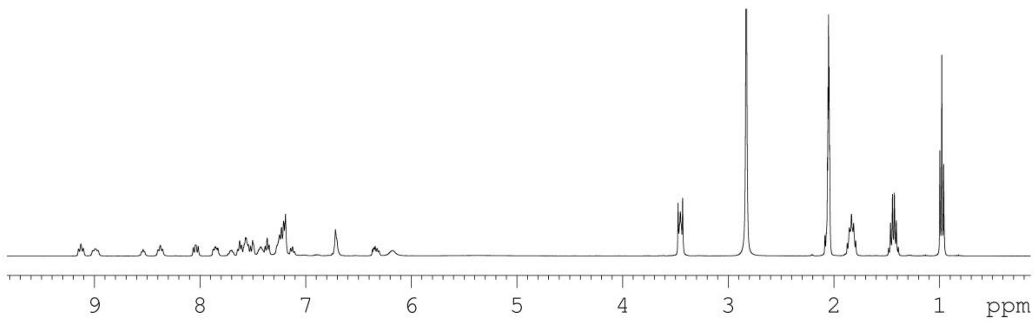

Figure S14 ^{1}H NMR spectrum of **5d** (acetone-d_6, 298 K)

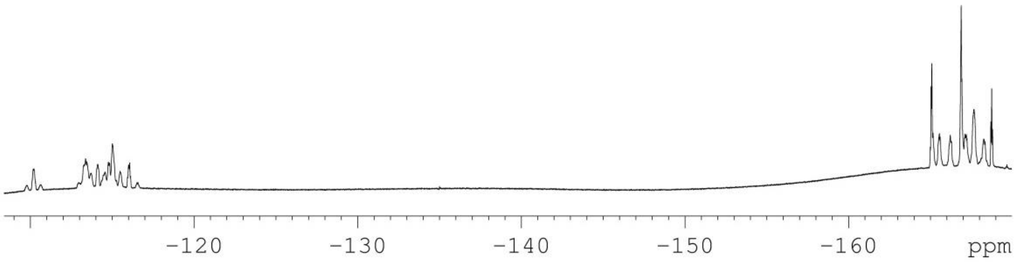

Figure S15 ^{19}F NMR spectrum of **5d** (acetone-d_6, 298 K)

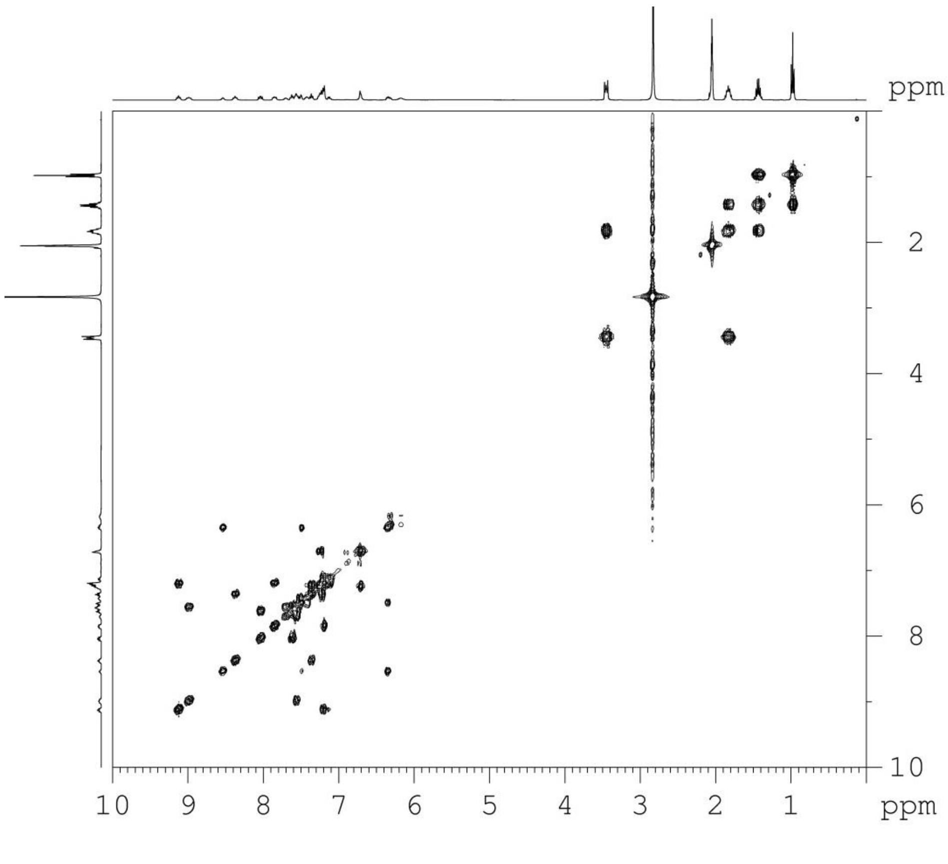

Figure S16 ^{1}H COSY spectrum of **5d** (acetone-d_6, 298 K)

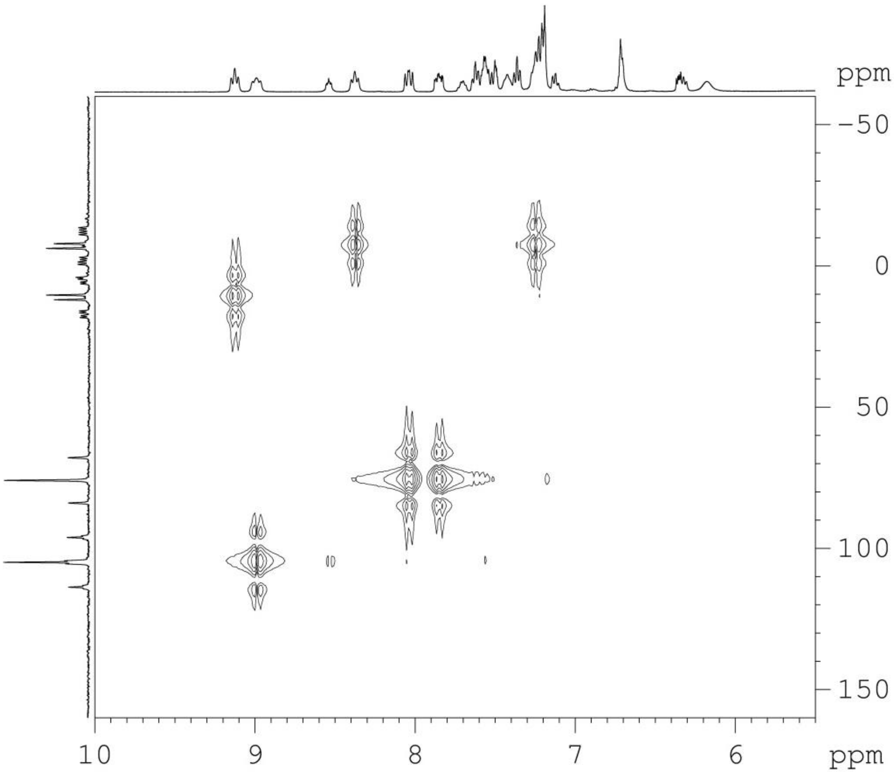

Figure S17 ^{1}H-^{31}P HMQC spectrum of **5d** (acetone-d_6, 298 K)

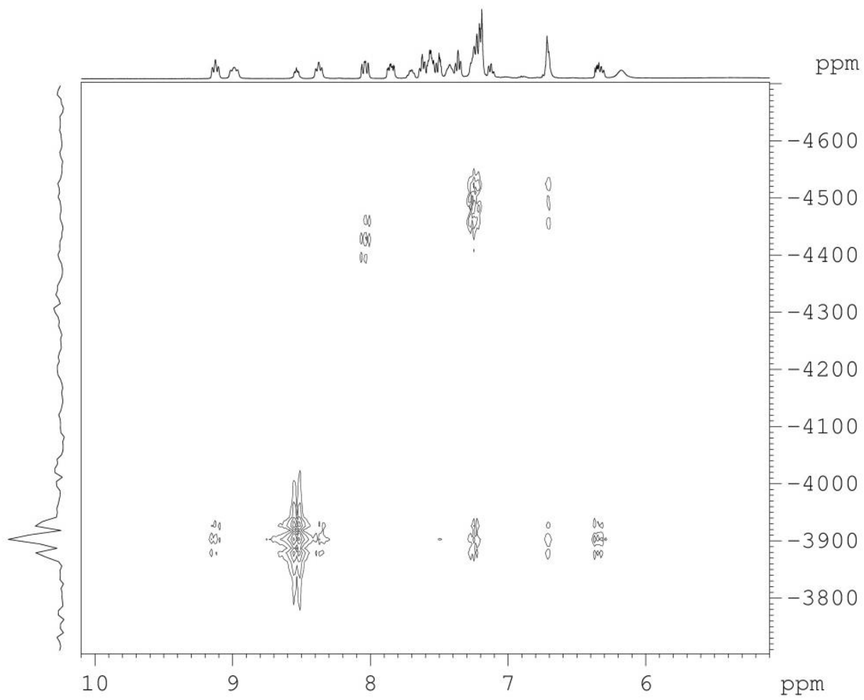

Figure S18 ^{1}H-^{195}Pt HMQC spectrum of **5d** (acetone-d_6, 298 K)

Table S1. Crystal data and structure refinement for complexes $[PPN][(C_6F_5)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{IV}(\kappa^2\text{-}S,S'\text{-}EtOCS_2)(\mu\text{-}PPh_2)_2Pt^{II}(C_6F_5)_2]\cdot 1.3Me_2CO\cdot 0.35n\text{-}C_6H_{14}$ (**3'b**$\cdot 1.3Me_2CO\cdot 0.35n\text{-}C_6H_{14}$) and $[N^nBu_4][(C_6F_5)_2Pt^{II}(\mu\text{-}PPh_2)_2Pt^{II}\{\kappa^2\text{-}N,P\text{-}\mu\text{-}(pymS)PPh_2\}(\mu\text{-}PPh_2)Pt^{II}(C_6F_5)_2]$ $3Me_2CO$ (**4d**$\cdot 3Me_2CO$).

	3'b$\cdot 1.3Me_2CO\cdot 0.35n\text{-}C_6H_{14}$	**4d**$\cdot 3Me_2CO$
Formula	$C_{111}H_{75}F_{20}NOP_6Pt_3S_2$ $\cdot 1.3Me_2CO\cdot 0.35n\text{-}C_6H_{14}$	$C_{92}H_{79}F_{20}N_3P_4Pt_3S$ $\cdot 3Me_2CO$
M_t	2759.59	2522.02
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	10.9730(1)	11.3413(2)
b/Å	22.5624(3)	20.1597(3)
c/Å	23.9417(3)	22.1094(3)
a/°	63.291(1)	94.278(1)
β/°	78.708(1)	103.612(1)
γ/°	83.442(1)	92.524(1)
V/Å^3	5190.15(12)	4889.45(12)
Z	2	2
D_c/g cm^{-3}	1.766	1.713
T/K	100(1)	100(1)
μ/mm^{-1}	4.256	4.458
F(000)	2702	2476
2θ range/°	8.4-58.7	8.4-58.6
Collected reflections	113426	85538
Unique reflections	25336	23566
R_{int}	0.0298	0.0448
R_1, wR_2^a ($I > 2\sigma(I)$)	0.0271, 0.0629	0.0346, 0.0809
R_1, wR_2^a (all data)	0.0318, 0.0650	0.0448, 0.0875
GOF $(F^2)^b$	1.061	1.022

^{a} $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$. $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. ^{b} Goodness-of-fit = $[\sum w (F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$.