Supplementary Material (ESI) for Chemical Communications

Supporting Information

Manuscript: H-Bonding Directs H_2O_2 Oxidation of Platinum(II) to a *cis*-Dihydroxo Platinum(IV) Complex

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Synthesis of Ligands and Complexes

The synthesis of the complexes [(6-aminobipy)$PtMe_2$] (**4**), [(4-aminobipy)$PtMe_2$] (**6**), [(2-methylphen)$PtMe_2$] (**7**) and [(2,9-dimethylphen)$PtMe_2$] (**8**) have been previously described.[S1, S2]

[S1] G. J. P. Britovsek, R. A. Taylor, G. J. Sunley, D. J. Law, and A. J. P. White, *Organometallics*, **2006**, *25*, 2074-2079.

[S2] A. Klein, E. J. L. McInnes, and W. Kaim, *J. Chem. Soc. Dalton Trans.*, **2002**, 2371-2378.

6,6'-diamino-2,2'-bipyridine

A 25 ml autoclave was loaded with 1.00 g (3.18 mmol) of 6,6'-dibromo-2,2'-bipy, to which 10 ml of ethylene glycol and 7.6 mg of copper(I)oxide was added. This was cooled to -78 ^oC and 10 ml of liquid ammonia was added to the solid mixture. The autoclave was sealed and allowed to warm to room temperature and immersed in an oil bath at 120 ^oC for 16 hours. After the autoclave had cooled and vented, the resultant red solution was poured from the autoclave into a beaker and the autoclave then flushed with 15 ml of water, which was added to the red solution. A further 20 ml of water was added to the mixture such that it had turned brown. The basic aqueous solution was extracted with 3 x 25 ml portions of dichloromethane. The combined extracts were washed with 2 x 15 ml potions of water and 1 x 15 ml saturated brine solution, treated with activated carbon, dried over magnesium sulphate and evaporated under reduced pressure. The resultant brown solid was then recrystallized from hot

chloroform. Typical yield: 35%. ^{1}H NMR ($(CD_3)_2CO$, δ): 5.36 (br, 4H, N*H*$_2$), 6.53 (d, 2H, *J* = 8.1 Hz, Ar–*H*), 7.46 (t, 2H, *J* = 7.6 Hz, Ar–*H*), 7.60 (d, 2H, *J* = 7.6 Hz, Ar–*H*). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$, δ): 108.8, 110.4, 138.4, 155.7, 159.9. MS (CI, *m/z* (%)): 187 (100) [$(M+H)^+$].

[(6,6'-diaminobipy)PtMe$_2$] 1

A Schlenk flask was loaded with 6,6'-diamino-2,2'-bipyridine (0.3773 g, 2.026 mmol) and $[PtMe_2(SMe_2)]_2$ (0.5814 g, 1.012 mmol) to which was added 15 ml of dry diethyl ether. After stirring for several minutes a yellow precipitate formed and the mixture was stirred overnight. The diethyl ether was removed by filtration and the remaining solid washed with 2 further portions of diethyl ether (10 ml). The bright yellow solid was subsequently dried under vacuum. Yield 0.71 g, (85%). ^{1}H NMR ($(CD_3)_2CO$, δ): 0.85 (s, 6H, $^{2}J_{PtH}$ = 88.2 Hz, PtMe), 6.28 (br, 4H, N*H*$_2$), 6.77 (m, 2H, Ar–*H*), 7.39 (dd, 2H, *J* = 0.9, 7.6 Hz, Ar–*H*), 7.64 (t, 2H, *J* = 7.9 Hz, Ar–*H*). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$, δ): -21.4 (Pt–*C*, $^{1}J_{PtC}$ = 817 Hz) 111.1 (C3, C5), 138.0 (C4), 156.6, 160.2. MS (FAB, *m/z* (%)): 411 (15) [M^+], 396 (45) [$(M\text{-}CH_3)^+$], 381 (85) [$(M\text{-}(CH_3)_2)^+$]. Anal. Calcd. For $C_{12}H_{16}N_4Pt$: C, 35.04; H, 3.92; N, 13.62. Found: C, 34.95; H, 3.77; N, 13.56.

[(6,6'-diaminobipy*)PtMe$_2$(OH)]$_3$ 2

A Schlenk flask was loaded with [(6,6'-diaminobipy)PtMe$_2$] **1** (283 mg, 0.689 mmol) in a glove box, to which 10 ml of dry acetone was added forming an orange solution. With vigorous stirring, 0.2 ml of aqueous H_2O_2 solution (35% w/v) was added to the solution dropwise, at which point a yellow solid precipitates from the yellow solution. The suspension was allowed to stir for 10 minutes. The acetone was removed by filtration and the remaining yellow solid washed with 2 x 20 ml of diethyl ether. The solid was dried under vacuum. Yield 230 mg. ^{1}H NMR (*d*$_7$-DMF, δ): -0.74 (br, 1H, PtO*H*), -0.01 (br, 1H, PtO*H*), 0.30 (br, 1H, PtO*H*), 0.54 (s, 3H, PtMe), 0.69 (s, 3H, PtMe), 0.73 (s, 3H, PtMe), 1.00 (s, 3H, PtMe), 1.05 (s, 3H, PtMe), 1.76 (s, 3H, PtMe), 5.58 (br, 1H, N*H*), 5.61 (br, 2H, N*H*), 5.66 (d, 1H, Ar–*H*), 6.55-6.67 (m, 5H, Ar–*H*), 6.77 (d, 1H, Ar–*H*), 6.84 (t, 1H, Ar–*H*), 6.88 (d, 1H, Ar–*H*), 7.10 (t, 1H, Ar–*H*), 7.21 (d, 1H, Ar–*H*), 7.29 (d, 1H, Ar–*H*), 7.32 (d, 1H, Ar–*H*), 7.49 (d,

1H, Ar–*H*), 7.52 (d, 1H, Ar–*H*), 7.58 (d, 1H, Ar–*H*), 7.61 (d, 1H, Ar–*H*), 7.81 (d, 1H, Ar–*H*). $^{13}C\{^1H\}$ NMR (d_7-DMF, δ): -5.2 (Pt–*C*), -5.1 (Pt–*C*), -4.0 (Pt–*C*), -3.2 (Pt–*C*), -3.0 (Pt–*C*), -1.6 (Pt–*C*), 106.0 (2 Ar–*C*), 106.4, 109.0, 109.1, 109.5, 112.0, 112.4 (2 Ar–*C*), 115.4, 117.1, 118.1, 133.6, 134.7, 135.0, 138.1, 138.3, 138.6, 153.3, 154.2, 154.6, 155.1, 155.4, 155.8, 163.3, 165.7, 165.8, 165.9. MS (FAB, *m/z* (%)): 855 (15) [$(2/3M)^+$], 428 (30) [$(1/3M)^+$], 410 (10) [$(1/3M\text{-}OH)^+$], 397 (30) [$(1/3M\text{-}2CH_3)^+$], 380 (100) [$(1/3M\text{-}2CH_3\text{-}OH)^+$]. Crystals suitable for X-ray analysis were grown by cooling a saturated acetone solution to -20 °C for two weeks.

[(6,6'-diaminobipy)PtMe$_2$(OH)$_2$] (*cis*-3)

To a solution of complex [(6,6'-diaminobipy)PtMe$_2$] **1** (10.4 mg, 0.025 mmol) in d_6-acetone (0.544 g) was added 0.02 ml of H_2O_2 (35 % in water), which results in the formation of a yellow precipitate. To the suspension, 0.2 ml H_2O was added, which results in complete dissolution to give a bright yellow solution. ^1H NMR ($(CD_3)_2CO/H_2O$, δ): 0.91 (s, 3H, $^2J_{PtH}$ = 68.0 Hz, PtMe axial), 1.71 (s, 3H, $^2J_{PtH}$ = 70.4 Hz, PtMe equatorial), 6.65-6.75 (m, 2H, Ar–*H*), 7.32 (d, 1H, Ar–*H*), 7.39 (m, 1H, Ar–*H*), 7.56 (m, 2H, Ar–*H*), 8.10 (br, 2H, N*H*$_2$). ^{13}C NMR ($(CD_3)_2CO/H_2O$, δ): -12.7 (Pt–*C*), -0.5 (Pt–*C*), 111.0, 112.3, 113.6, 114.4, 138.9, 139.6, 152.7, 155.4, 161.5, 162.3.

[(6-aminobipy)PtMe$_2$(OH)$_2$] (*cis*-5' and *trans*-5)

A Schlenk flask was loaded with [Pt(6-aminobipy)Me$_2$] **4** (20.6 mg, 0.052 mmol) in a glove box, to which 10 ml of dry acetone was added forming a yellow solution. With vigorous stirring, 0.2 ml of aqueous H_2O_2 solution (35% w/v) was added to the solution dropwise, at which point the yellow acetone solution became pale yellow. The solution was allowed to stir for 10 minutes after which point all volatiles were removed. A 1:1 mixture of *cis*:*trans* isomers *cis*-**5'** and *trans*-**5** is formed. ^1H NMR (CD_3OD, δ): 1.00 (s, 3H, $^2J_{PtH}$ = 68.6 Hz, PtMe *cis*-**5'** axial), 1.62 (s, 3H, $^2J_{PtH}$ = 68.4 Hz, PtMe *cis*-**5'** equatorial), 1.78 (s, 3H, $^2J_{PtH}$ = 73.8 Hz, PtMe *trans*-**5'** equatorial), 1.80 (s, 3H, $^2J_{PtH}$ = 71.4 Hz, PtMe *trans*-**5'** equatorial), 6.78 (d, 1H, *J* = 8.5 Hz, Ar–*H*), 6.86 (dd, 1H, *J* = 1.9 ,7.5 Hz, Ar–*H*), 7.54-7.72 (m, 6H, Ar–*H*), 8.15 (m, 2H, Ar–*H*), 8.35 (d, 1H, *J* = 7.9 Hz, Ar–*H*), 8.40 (d, 1H, *J* = 8.2 Hz, Ar–*H*), 8.71 (d, 1H, $^3J_{PtH}$ = 36.6 Hz, *J* = 5.7 Hz, H6' *cis*-**5'**), 8.91 (d, 1H, *J* = 4.6 Hz, H6' *trans*-**5**). ^{13}C NMR (CD_3OD, δ): -12.6 (Pt–*C*), -6.6 (Pt–*C*), 0.0 (Pt–*C*), 5.1 (Pt–*C*), 112.1, 113.8, 114.8,

116.7, 125.0, 125.1, 126.8, 127.8, 139.5, 140.3, 140.7, 141.2, 147.5, 149.4, 150.8, 154.0, 159.0, 159.6, 161.8, 163.6.

[(4-aminobipy)PtMe$_2$(OH)$_2$] (*trans*-9)

A Schlenk flask was loaded with [Pt(4-aminobipy)Me$_2$] **6** (31 mg, 0.0782 mmol) in a glove box, to which 20 ml of dry acetone was added forming a yellow solution. With vigorous stirring, 0.2 ml of aqueous H_2O_2 solution (35% w/v) was added to the solution dropwise, at which point the yellow acetone solution became very pale yellow The solution was allowed to stir for 10 minutes after which point all volatiles were removed. The remaining solid was dissolved in 2 ml of methanol, treated with charcoal and filtered through celite. All volatiles were removed leaving a pale yellow green solid. Yield 20 mg (60%). ^{1}H NMR (CD_3OD, δ): 1.59 (s, 3H, $^2J_{PtH}$ = 68.7 Hz, PtMe), 1.69 (s, 3H, $^2J_{PtH}$ = 70.8 Hz, PtMe), 6.82 (dd, 1H, *J* = 2.4, 6.4 Hz, Ar–*H*), 7.58 (d, 1H, *J* = 2.4 Hz, Ar–*H*), 7.73 (t, 1H, *J* = 5.5 Hz, Ar–*H*), 8.17 (td, 1H *J* = 1.5, 7.9 Hz, Ar–*H*), 8.36 (m, 2H, Ar–*H*), 8.95 (d, 1H, *J* = 5.2 Hz, Ar–*H*). ^{13}C{^{1}H} NMR (CD_3OD, δ): -4.0 (Pt–*C*, $^1J_{PtC}$ = 640 Hz), -4.1 (Pt–*C*, $^1J_{PtC}$ = 640 Hz), 109.4, 111.6, 124.2, 127.5, 140.9, 147.7, 148.2, 156.7, 157.9, 158.6. MS (FAB, *m/z* (%)): 413 (20) [(M-OH)$^+$]. Anal. Calcd. For $C_{12}H_{17}N_3O_2Pt$: C, 33.49; H, 3.98; N, 9.76. Found: C, 33.33; H, 4.09; N 9.65.

[(2-methylphen)PtMe$_2$(OH)$_2$] (*trans*-10)

A Schlenk flask was loaded with [(2-methylphen)PtMe$_2$] **7** (150 mg, 0.358 mmol) in a glove box, to which 20 ml of dry acetone was added forming an orange suspension. With vigorous stirring, 0.25 ml of aqueous H_2O_2 solution (35% w/v) was added to the solution dropwise, at which point the orange suspension produced a grey precipitate. The solution was allowed to stir for 1.5 hr after which point all volatiles were removed. The remaining solid was dissolved in 7 ml of methanol, treated with charcoal and filtered through celite. All volatiles were removed leaving a pale grey solid. Yield 135 mg (83%). ^{1}H NMR (CD_3OD, δ) *trans*: 1.98 (s, 3H, $^2J_{PtH}$ = 72.2 Hz, PtMe), 2.04 (s, 3H, $^2J_{PtH}$ = 73.3 Hz, PtMe), 3.22 (s, 3H, 2-C*H*$_3$), 7.92 (d, 1H, *J* = 8.2 Hz, H3), 8.10 (dd, 1H, *J* = 5.1, 8 Hz, H8), 8.13 (AB quartet, 2H, H5, H6) 8.62, (d, 1H, *J* = 8.5 Hz, H4), 8.77 (dd, 1H, *J* = 1.2, 8 Hz, H7), 9.34 (dd 1H, *J* = 5.1, 1.2 Hz, H9). ^{13}C{^{1}H} NMR (CD_3OD, δ): -4.4 (Pt–*C*), 0.5 (Pt–*C*), 26.6 (2-*C*H$_3$), 126.2 (C8), 127.7, 129.1 (2 Ar–*C*H), 130.9, 132.9, 140.0 (C4), 140.5 (C7), 147.7, 148.3, 148.4 (C9), 165.2 (C2). MS

(FAB, *m/z* (%)): 453 (17) [M^+], 436 (90) [$(M\text{-}OH)^+$]. Anal. Calcd. For $C_{15}H_{18}N_2O_2Pt$: C, 39.74; H, 4.00; N, 6.18. Found: C, 39.76; H, 3.91; N, 6.11.

Reaction of [(2,9-dimethylphen)PtMe$_2$] with Hydrogen Peroxide

To a solution of complex [(2,9-dimethylphen)PtMe$_2$] **8** (8.8 mg, 0.020 mmol) in d_6-acetone (0.502 g) was added 0.02 ml of H_2O_2 (35 % in water), which resulted in the formation of a colourless solution. Volatiles were removed using a stream of dinitrogen gas and the residue taken up in CD_3OD. Analysis by ^{1}H NMR showed the presence of 2,9-dimethylphen and a complex assigned as [(2,9-dimethylphen)PtMe$_2$(OH)$_2$] *trans*-**11** in a 3:1 ratio. ^{1}H NMR (CD_3OD, δ):1.92 (s, 6H, $^2J_{PtH}$ = 72.8 Hz, PtMe), 7.80 (obscured by 2,9-dimethylphen signals) 7.98 (s, 2H, Ar–*H*), 8.52 (d, 2H, Ar–*H*).

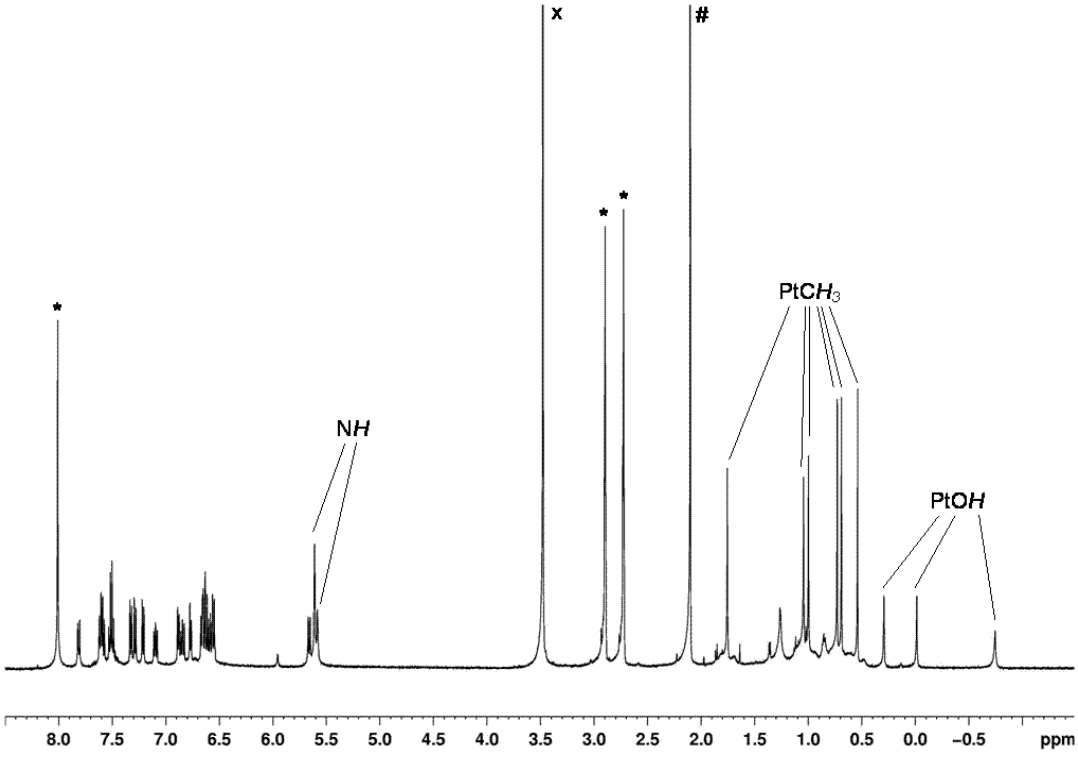

Figure S.1 ^{1}H NMR spectrum of [Pt(6,6'-diaminobipy*)Me$_2$(OH)]$_3$ **2** in d_7-DMF. Solvent impurities: DMF (*), acetone (#) water (x).

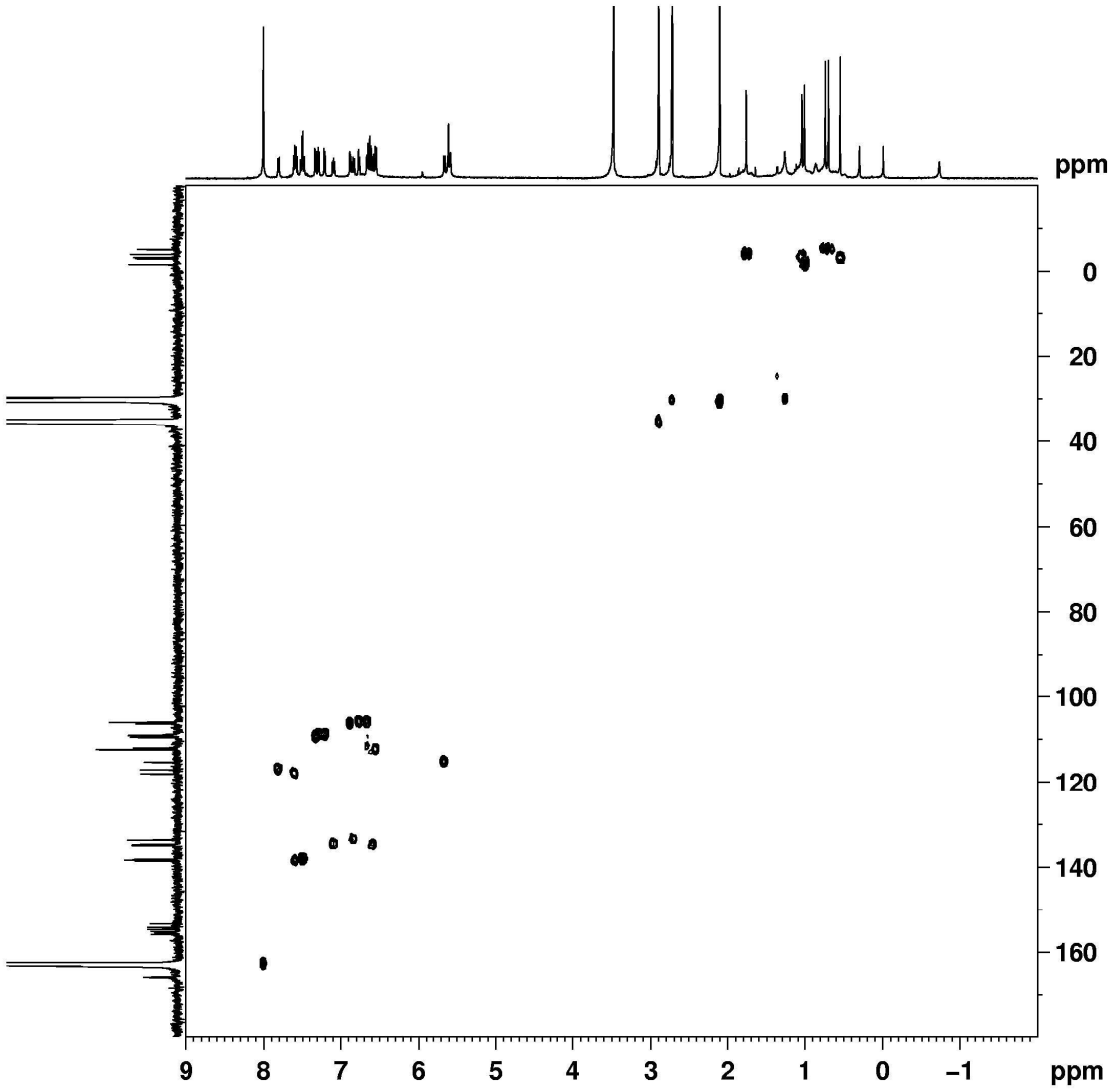

Figure S.2 HMQC spectrum of [Pt(6,6'-diaminobipy*)Me_2(OH)]$_3$ **2** in d^7-DMF

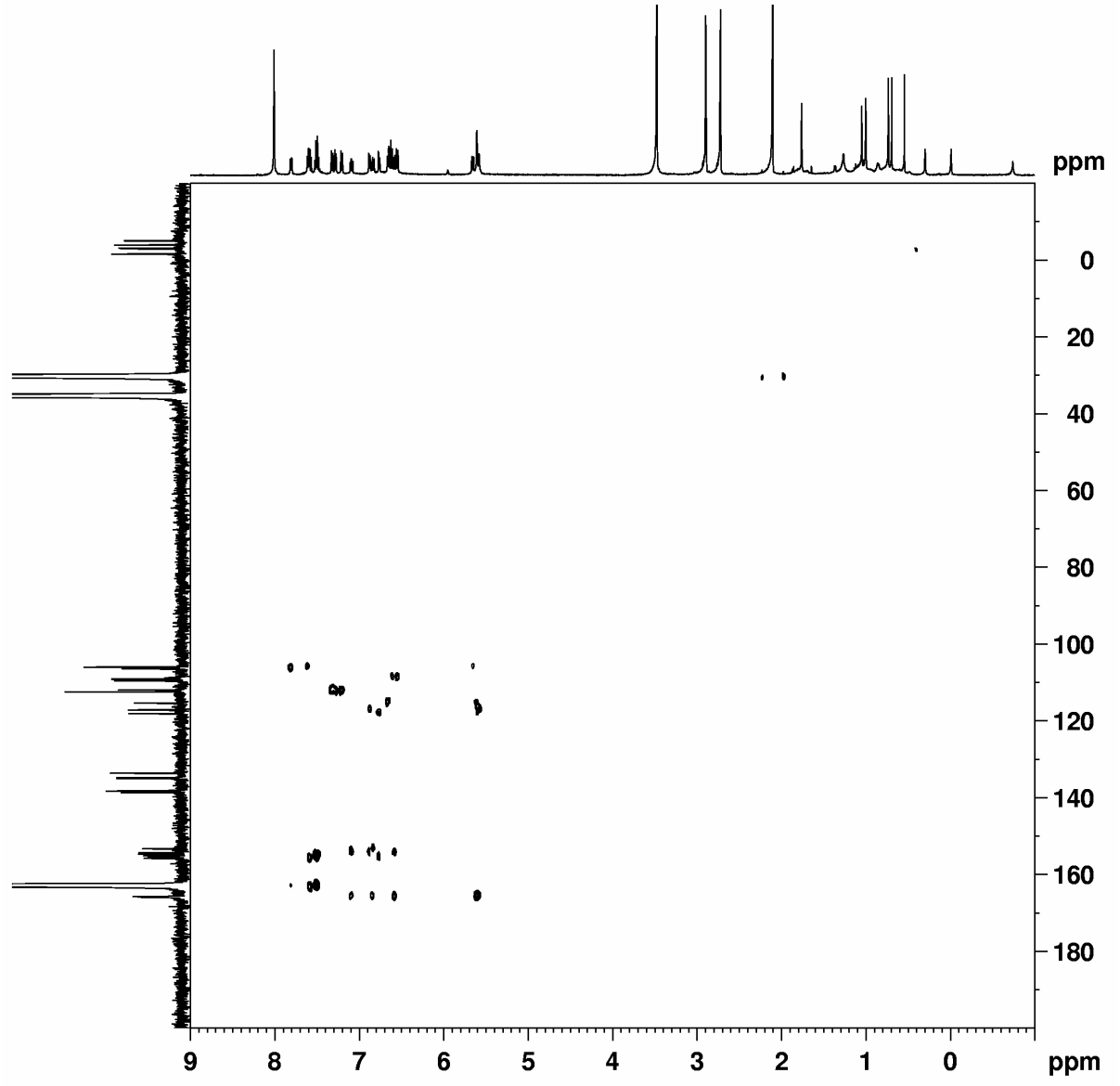

Figure S.3 HMBC spectrum of [Pt(6,6'-diaminobipy*)Me_2(OH)]$_3$ **2** in d^7-DMF

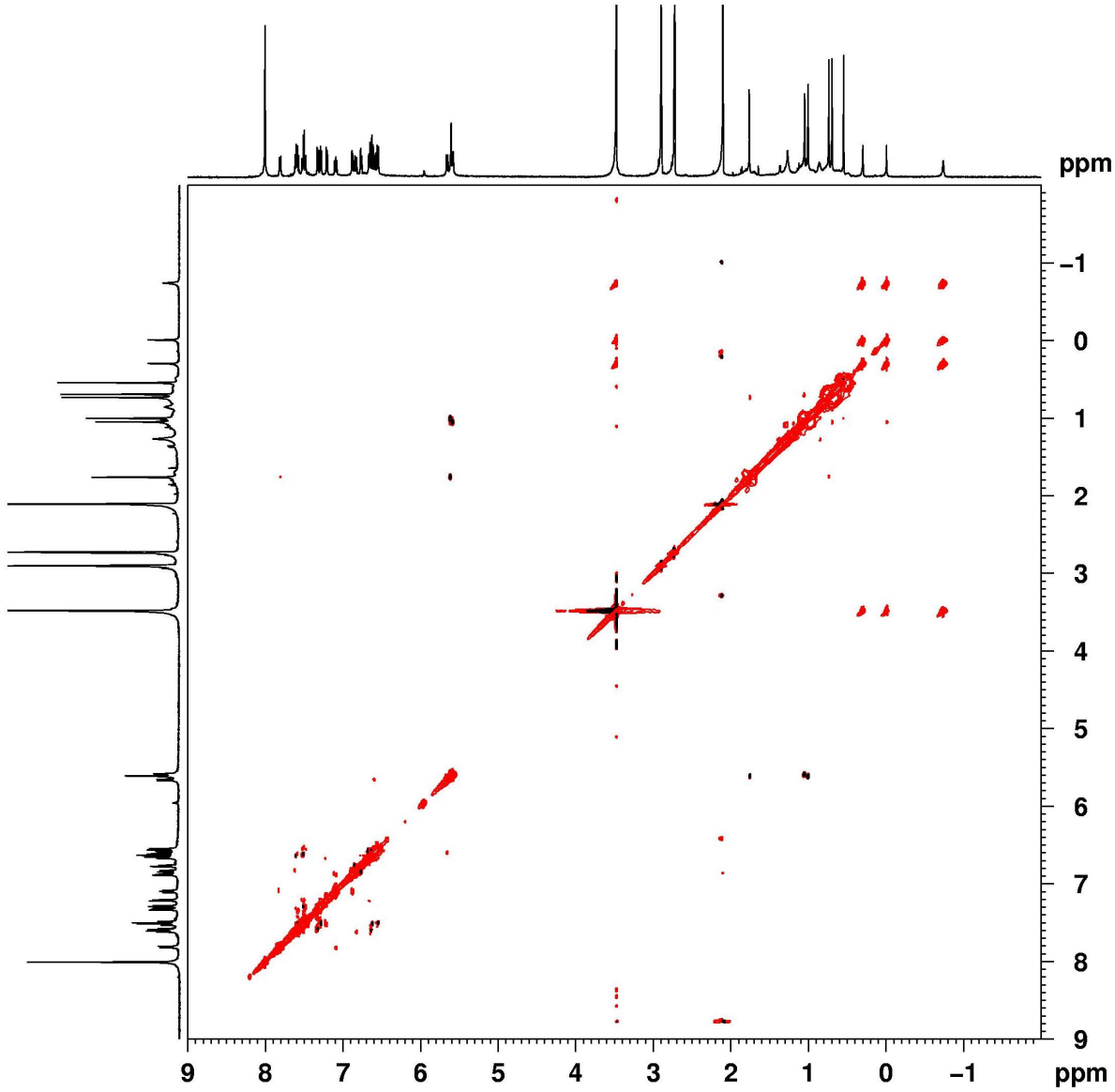

Figure S.4 NOESY spectrum of [Pt(6,6'-diaminobipy*)Me_2(OH)]$_3$ **2** in d^7-DMF

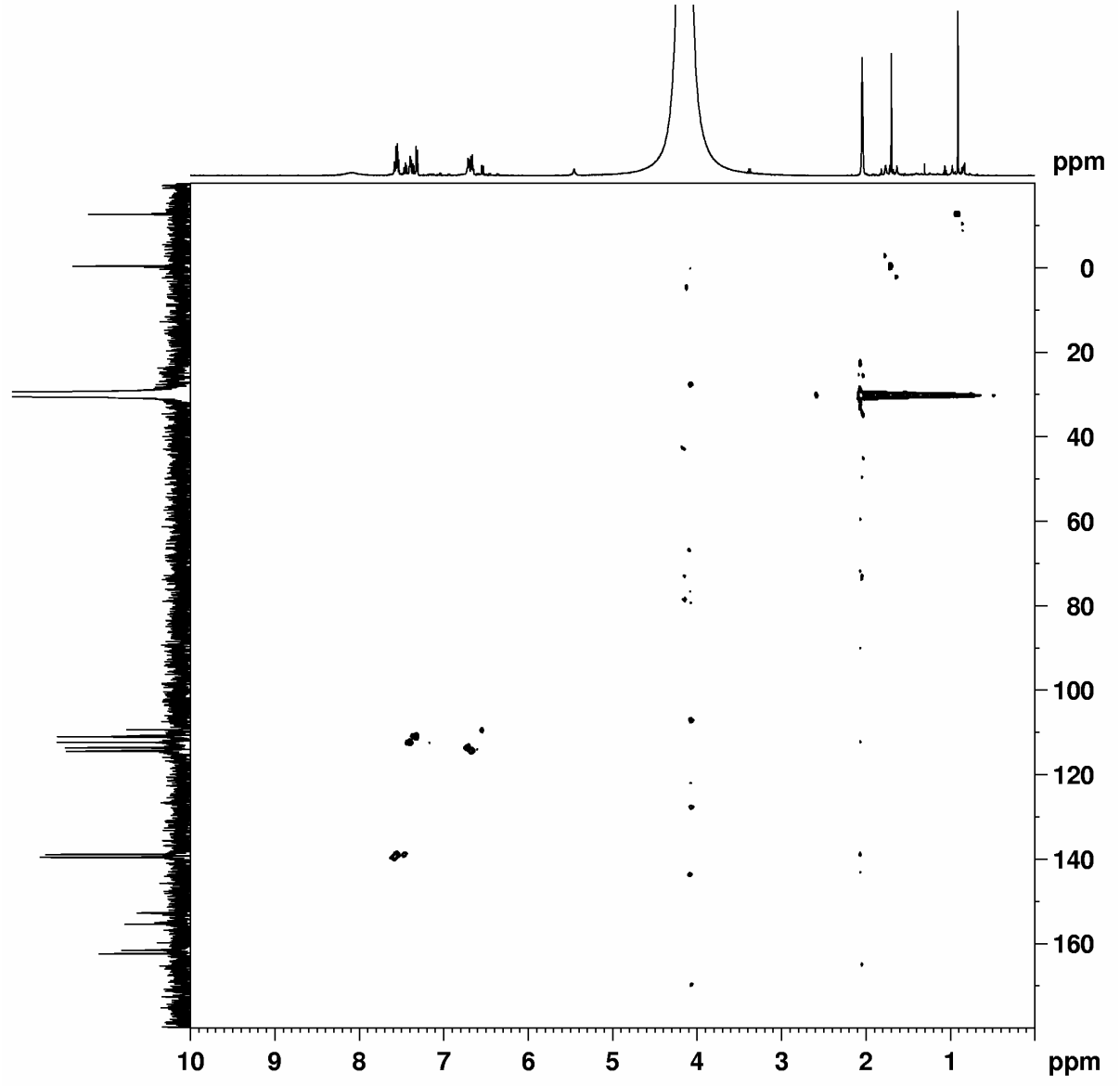

Figure S.5 HSQC spectrum of [(6,6'-diaminobipy)$PtMe_2(OH)_2$] *cis*-**3** in d^6-acetone/H_2O

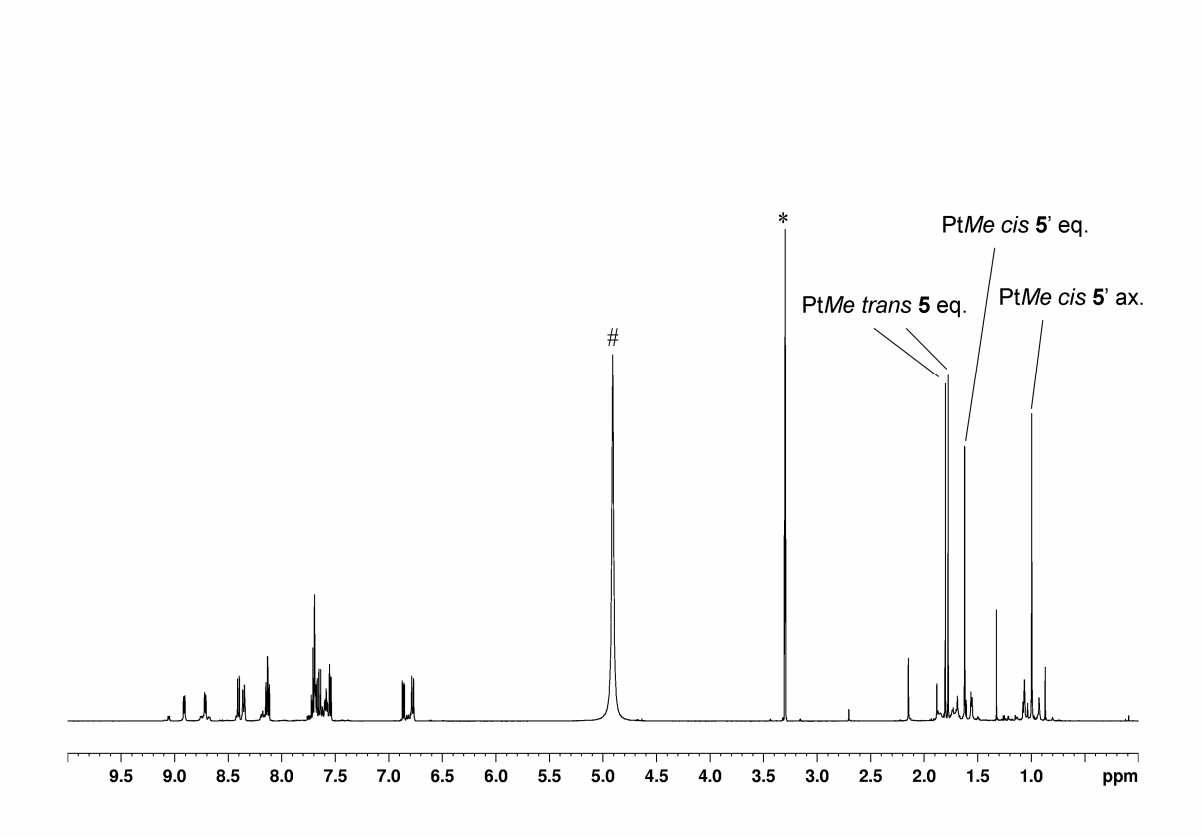

Figure S.6 ^{1}H NMR spectrum of [(6-aminobipy)$PtMe_2(OH)_2$] *cis*-**5'** and *trans*-**5** in CD_3OD (*), # = H_2O.

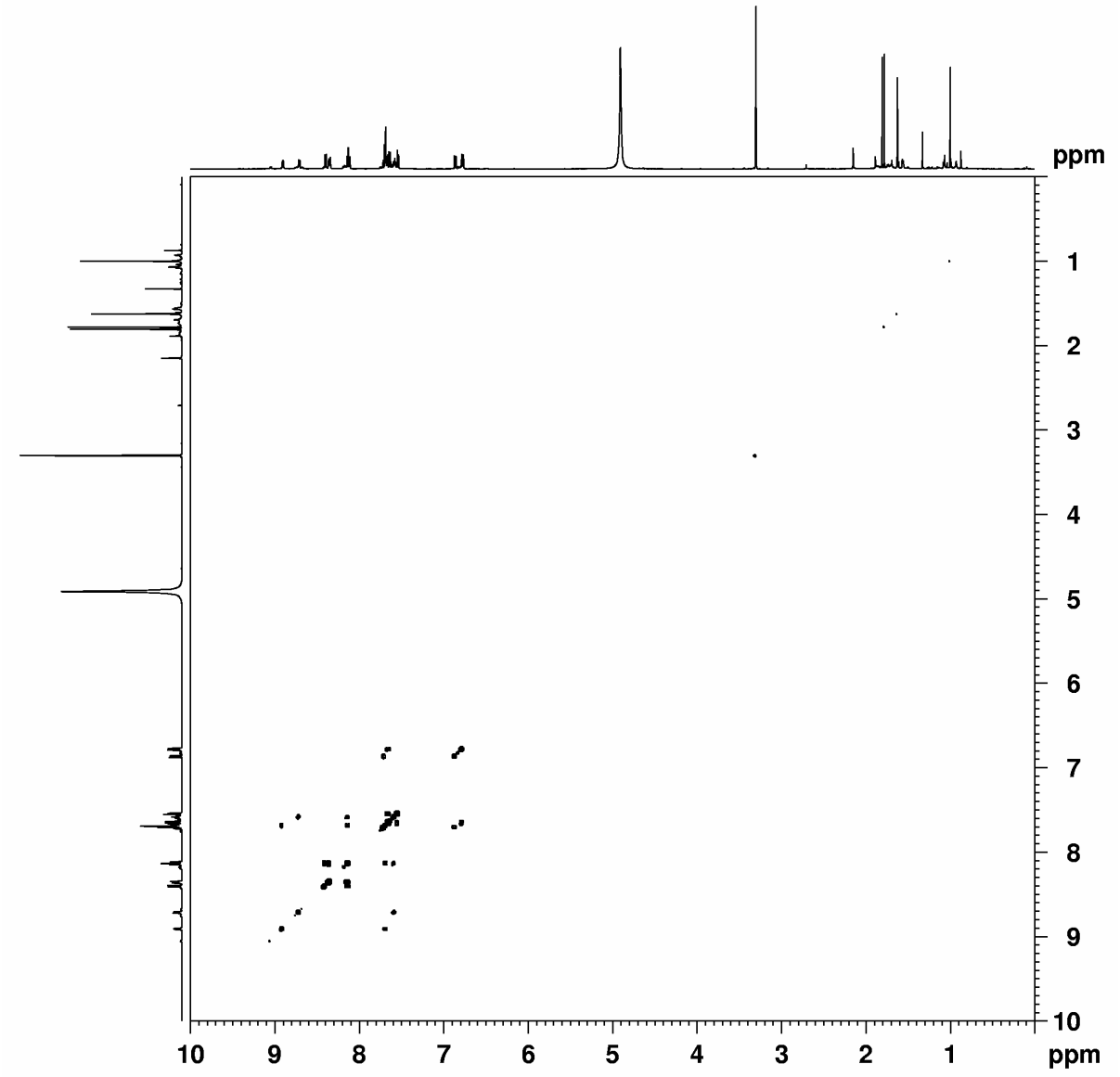

Figure S.7 COSY spectrum of [(6-aminobipy)$PtMe_2(OH)_2$] *cis*-**5'** and *trans*-**5** in CD_3OD.

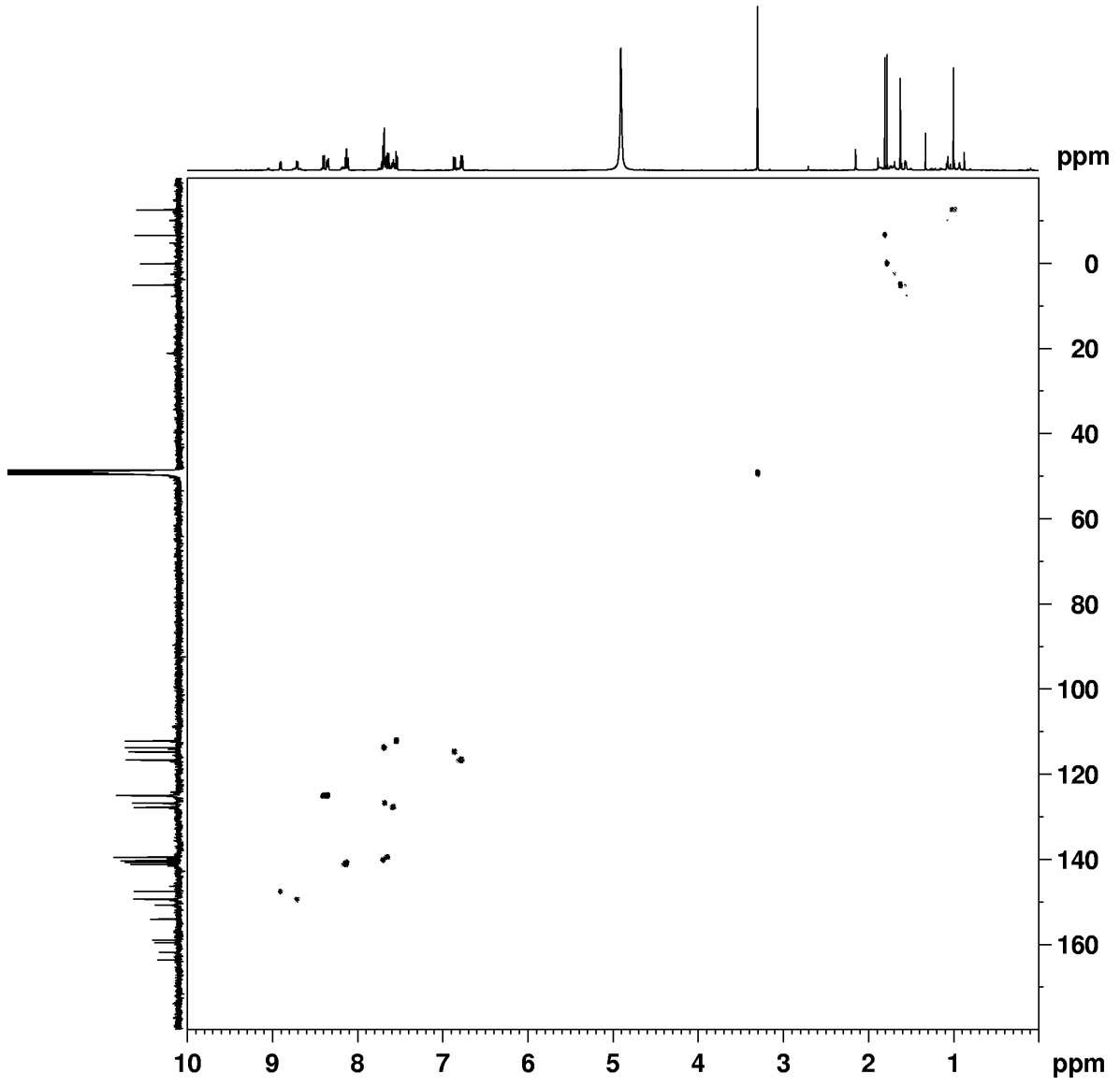

Figure S.8 HSQC spectrum of [(6-aminobipy)$PtMe_2(OH)_2$] *cis*-**5'** and *trans*-**5** in CD_3OD.

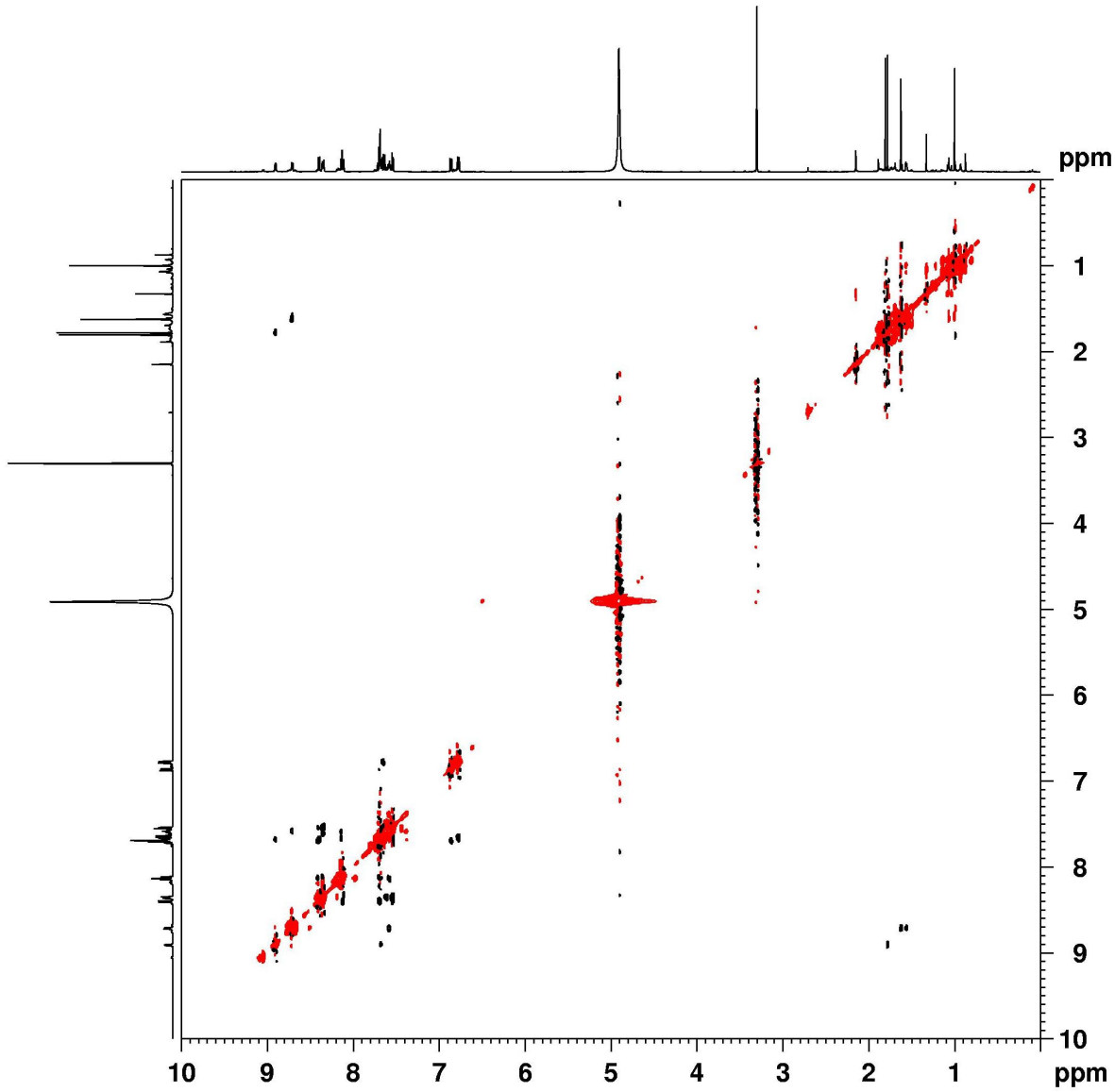

Figure S.9 NOESY spectrum of [(6-aminobipy)$PtMe_2(OH)_2$] *cis*-**5'** and *trans*-**5** in CD_3OD.

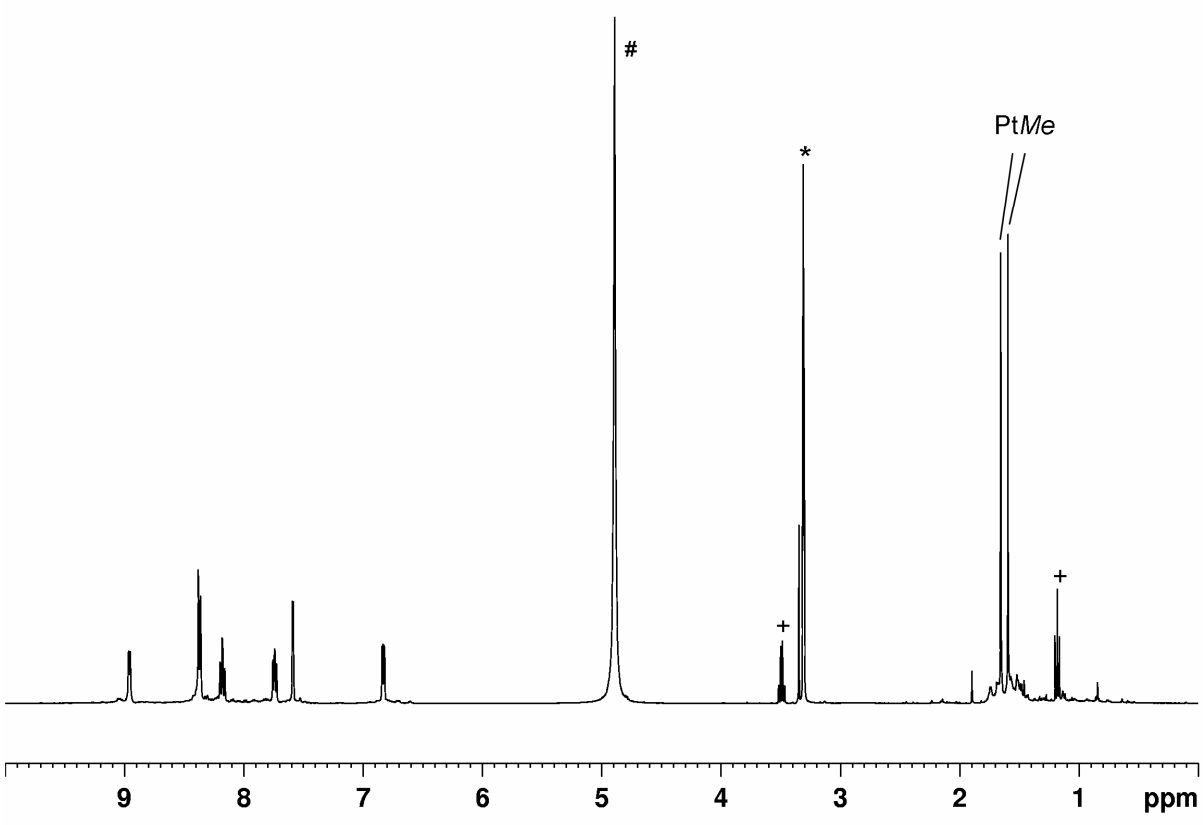

Figure S.10 ^{1}H NMR spectrum of [(4-aminobipy)PtMe$_2$(OH)$_2$] *trans*-**9** in CD_3OD (*). # = H_2O, + = Et_2O.

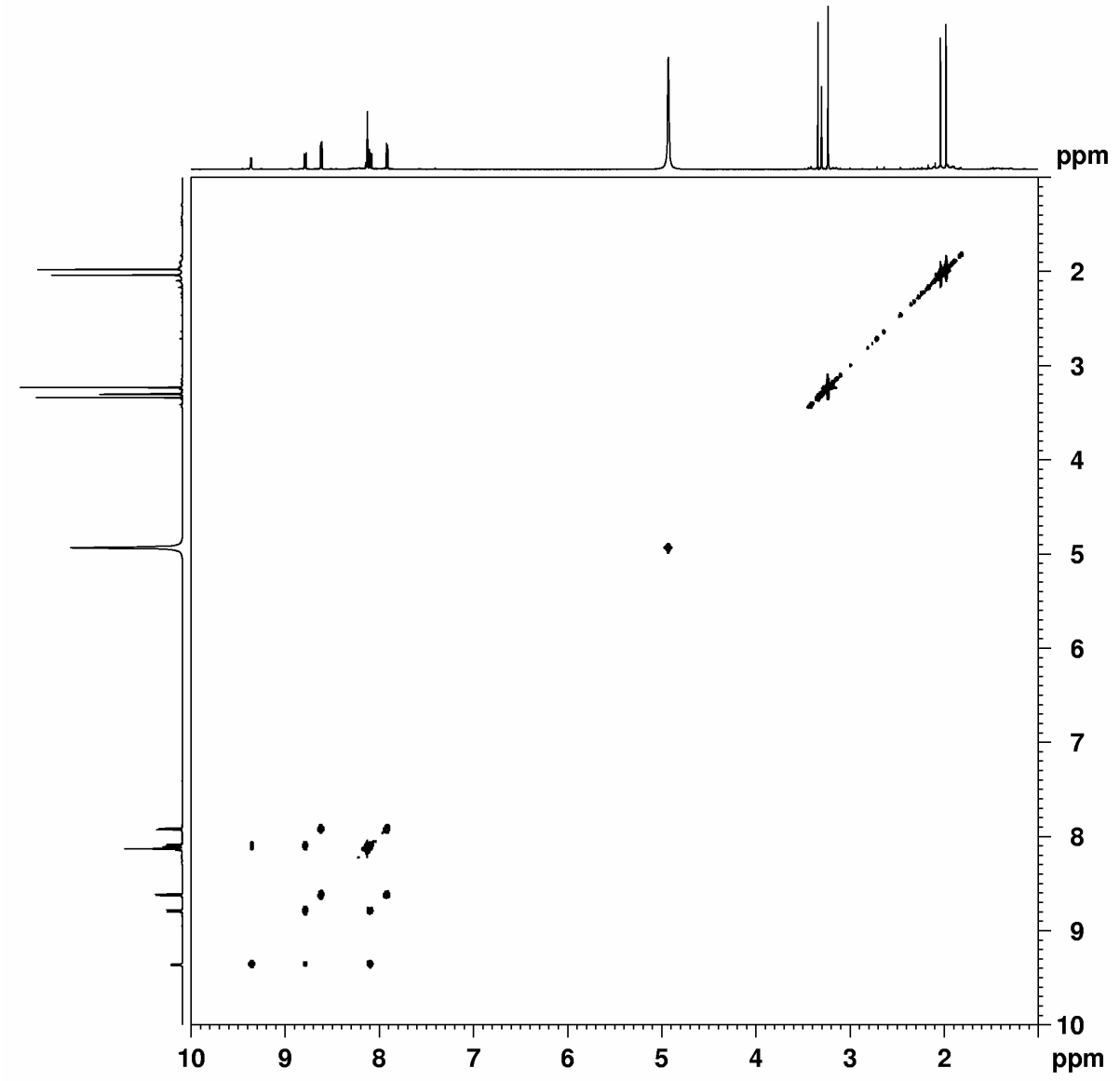

Figure S.11 COSY spectrum of [(2-methylphen)$PtMe_2(OH)_2$] *trans*-**10** in CD_3OD

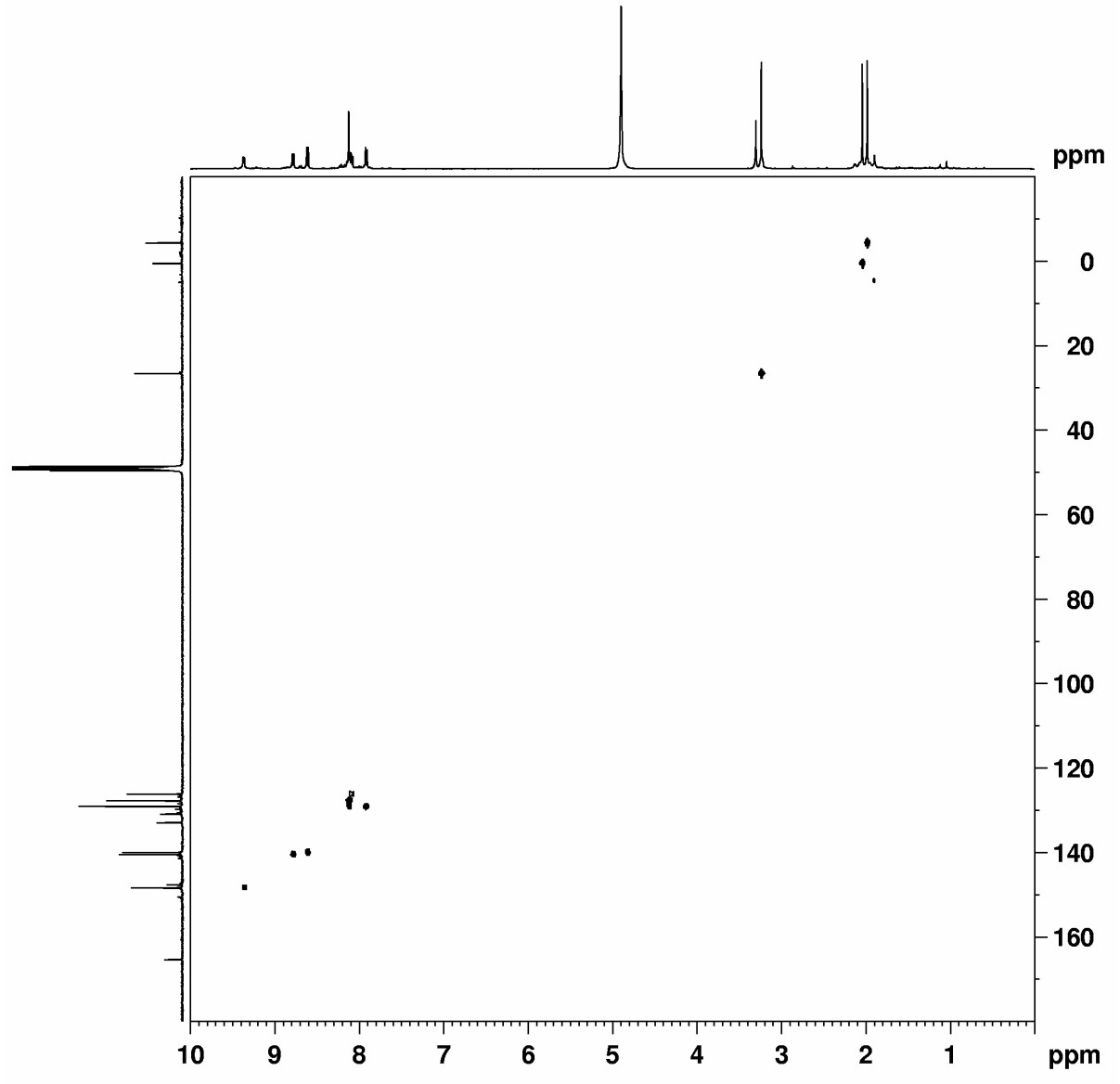

Figure S.12 HMQC spectrum of [(2-methylphen)$PtMe_2(OH)_2$] *trans*-**10** in CD_3OD

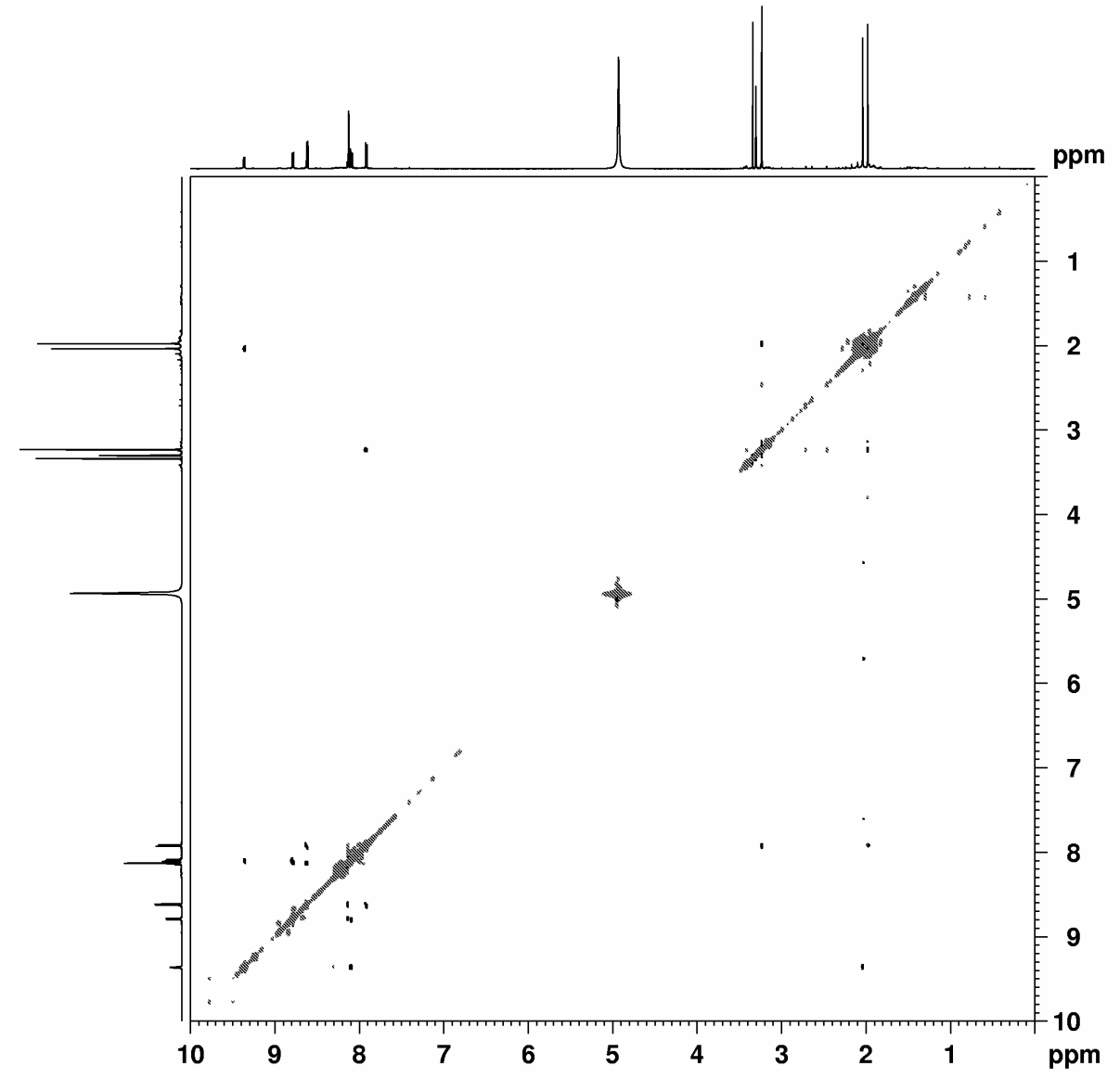

Figure S.13 NOESY spectrum of [(2-methylphen)$PtMe_2(OH)_2$] *trans*-**10** in CD_3OD

X-Ray Crystallography

Table S1. Selected bond lengths (Å) and angles (°) for complex **2**.

Pt(1)–O(1)	**2.014(13)**	**Pt(1)–N(1)**	**2.155(17)**
Pt(1)–N(12)	**2.050(15)**	**Pt(1)–C(15)**	**2.042(19)**
Pt(1)–C(16)	**2.05(2)**	**Pt(1)–N(54)**	**2.156(14)**
Pt(2)–O(2)	**2.008(12)**	**Pt(2)–N(14)**	**2.160(15)**
Pt(2)–N(21)	**2.172(14)**	**Pt(2)–N(32)**	**2.042(15)**
Pt(2)–C(35)	**2.036(18)**	**Pt(2)–C(36)**	**2.037(18)**
Pt(3)–O(3)	**2.020(12)**	**Pt(3)–N(34)**	**2.140(14)**
Pt(3)–N(41)	**2.170(15)**	**Pt(3)–N(52)**	**2.050(13)**
Pt(3)–C(55)	**2.05(2)**	**Pt(3)–C(56)**	**2.05(2)**
O(1)–Pt(1)–N(1)	**96.0(7)**	**O(1)–Pt(1)–N(12)**	**174.9(6)**
O(1)–Pt(1)–C(15)	**83.2(8)**	**O(1)–Pt(1)–C(16)**	**87.6(8)**
O(1)–Pt(1)–N(54)	**95.9(6)**	**N(1)–Pt(1)–N(12)**	**79.0(6)**
N(1)–Pt(1)–C(15)	**173.4(7)**	**N(1)–Pt(1)–C(16)**	**87.4(8)**
N(1)–Pt(1)–N(54)	**90.6(6)**	**N(12)–Pt(1)–C(15)**	**101.9(8)**
N(12)–Pt(1)–C(16)	**92.9(8)**	**N(12)–Pt(1)–N(54)**	**83.4(5)**
C(15)–Pt(1)–C(16)	**86.0(9)**	**C(15)–Pt(1)–N(54)**	**96.0(7)**
C(16)–Pt(1)–N(54)	**176.1(8)**	**O(2)–Pt(2)–N(14)**	**88.8(6)**
O(2)–Pt(2)–N(21)	**96.7(6)**	**O(2)–Pt(2)–N(32)**	**174.7(6)**
O(2)–Pt(2)–C(35)	**83.2(7)**	**O(2)–Pt(2)–C(36)**	**89.4(8)**
N(14)–Pt(2)–N(21)	**100.3(6)**	**N(14)–Pt(2)–N(32)**	**89.8(6)**
N(14)–Pt(2)–C(35)	**90.3(7)**	**N(14)–Pt(2)–C(36)**	**176.1(8)**
N(21)–Pt(2)–N(32)	**78.6(6)**	**N(21)–Pt(2)–C(35)**	**169.3(7)**
N(21)–Pt(2)–C(36)	**83.3(8)**	**N(32)–Pt(2)–C(35)**	**101.9(7)**
N(32)–Pt(2)–C(36)	**92.4(8)**	**C(35)–Pt(2)–C(36)**	**86.0(8)**
O(3)–Pt(3)–N(34)	**96.1(5)**	**O(3)–Pt(3)–N(41)**	**95.8(5)**
O(3)–Pt(3)–N(52)	**174.4(5)**	**O(3)–Pt(3)–C(55)**	**85.2(6)**
O(3)–Pt(3)–C(56)	**87.8(6)**	**N(34)–Pt(3)–N(41)**	**90.2(5)**
N(34)–Pt(3)–N(52)	**86.2(5)**	**N(34)–Pt(3)–C(55)**	**94.9(7)**
N(34)–Pt(3)–C(56)	**176.0(7)**	**N(41)–Pt(3)–C(55)**	**174.6(7)**
N(41)–Pt(3)–N(52)	**79.1(5)**	**N(41)–Pt(3)–C(56)**	**88.7(7)**
N(52)–Pt(3)–C(55)	**99.6(7)**	**N(52)–Pt(3)–C(56)**	**89.8(7)**
C(55)–Pt(3)–C(56)	**86.1(8)**		

The quality of the structure did not allow a reliable location of the hydrogen atoms. The identification of the hydroxy groups within each platinum coordination sphere (as distinct from the methyl groups) was performed by considering four factors. These were i) the thermal ellipsoids of the three possible sites in each metal coordination sphere when they

were all refined as carbon atoms; ii) the change in the *R*-factor when the proposed sites were refined as oxygen instead of carbon; iii) the Pt–X bond lengths to each of the possible sites; and iv) the potential involvement of these sites in hydrogen bonding interactions.

Table S2. Ueq values for potential hydroxy oxygen atoms in the structure of **2** when all refined as carbon (row **A**) and when X(1), X(2) and X(3) refined as oxygen (row **B**).

	X(1)	**X(15)**	**X(16)**	**X(2)**	**X(35)**	**X(36)**	**X(3)**	**X(55)**	**X(56)**
A	0.013	0.033	0.041	0.003	0.028	0.034	0.003	0.027	0.025
B	0.037	0.032	0.040	0.023	0.027	0.033	0.020	0.027	0.024

The entries in Table S2 are the Ueq values for each of the atoms. The results reported in row **A** are for all nine atoms refined as being carbon atoms, but with no associated protons included. The results in row B are for atoms X(1), X(2) and X(3) treated as oxygen atoms and the rest as carbon atoms (again no associated protons were included). From row **A** it is clear to see X(1), X(2) and X(3) stand out as having noticeably lower Ueq's when refined as carbon, and much more closely matching Ueq's when refined as oxygen (row **B**). The *R*-factors for the two runs were $R_1 = 0.155$ for row **A**, and $R_1 = 0.153$ for row **B**, again showing a preference (albeit small) for row **B**.

Unfortunately, the estimated standard deviations of the Pt–X bond lengths to the nine potential hydroxy sites are sufficiently high that none of the differences between the bonds are statistically significant (Table S3). Despite this, however, a potential pattern can be discerned and used as a guide. This pattern is that at each metal centre there are two bonds of *ca.* 2.04 Å and one bond of *ca.* 2.01 Å. In each case the apparently shorter bond is to the same atom identified above as being the potential hydroxy oxygen atom on the basis of its smaller thermal ellipsoid when refined as a carbon atom (*vide supra*).

Table S3. Pt–X bond lengths (Å) in the structure of **2**, where X is one of the nine potential hydroxy oxygen atoms.

Pt(1)–O(1)	2.014(13)	Pt(1)–C(15)	2.042(19)
Pt(1)–C(16)	2.05(2)	Pt(2)–O(2)	2.008(12)
Pt(2)–C(35)	2.036(18)	Pt(2)–C(36)	2.037(18)
Pt(3)–O(3)	2.020(12)	Pt(3)–C(55)	2.05(2)
Pt(3)–C(56)	2.05(2)		

All the above pieces of evidence are pointing in the same direction, and as it happens the indicated potential oxygen atom sites are all proximal to NH_2 groups to which hydrogen bonding interactions can easily be envisaged (see main text) with N···O separations of 2.68(3), 2.77(2) and 2.73(2) Å for O(1), O(2) and O(3) respectively. It thus seems highly likely that O(1), O(2) and O(3) are indeed oxygen atoms, and that C(15), C(16), C(35), C(36), C(55) and C(56) are all carbon atoms.

Despite the relatively high estimated standard deviations, an interesting pattern can be seen in the Pt–N bond lengths (see Table S1), with those to the bridging N–H nitrogen atoms N(14), N(34) and N(54) [Pt(2)–N(14) 2.160(15), Pt(3)–N(34) 2.140(14), Pt(1)–N(54) 2.156(14) Å] being the same (within statistical significance) as those to the bipyridine nitrogen centres N(1), N(21) and N(41) [Pt(1)–N(1) 2.155(17), Pt(2)–N(21) 2.172(14), Pt(3)–N(41) 2.170(15) Å], whilst those to the other bipyridine nitrogen atoms N(12), N(32) and N(52) are statistically significantly shorter [Pt(1)–N(12) 2.050(15), Pt(2)–N(32) 2.042(15), Pt(3)–N(52) 2.050(13) Å]. We believe that these differences are the result of the strong *trans* effect of the opposite methyl ligands, compared to the weak *trans* effect of the hydroxo ligand.

It is important to note that no geometric constraints or restraints were applied to the triplatinum complex, and that it shows no signs of disorder, though some of the thermal ellipsoids are less than ideal. Thus, the apparent distortions of the bipyridyl ring systems may indeed be real, though the large e.s.d.s prohibit any meaningful discussion of the associated bond lengths and angles.

Two included acetone solvent molecules were located in the asymmetric unit. One of these was found to be disordered, and two partial occupancy orientations were identified (of *ca.* 58 and 42% occupancy) and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. The non-hydrogen atoms of the ordered acetone were also refined anisotropically.

No other species were found to be present in the structure (*i.e.* no counterions), so the triplatinum complex must be neutral. Since no protons were located from ΔF maps, and the e.s.d.s of the bond lengths are rather high, the assignment of O(1), O(2) and O(3) being

hydroxy groups, N(13), N(33) and N(53) being NH_2 groups, and N(14), N(34) and N(54) being NH units, cannot be confirmed by the structural results.

Figure S14 The molecular structure of **2** (50% probability ellipsoids).

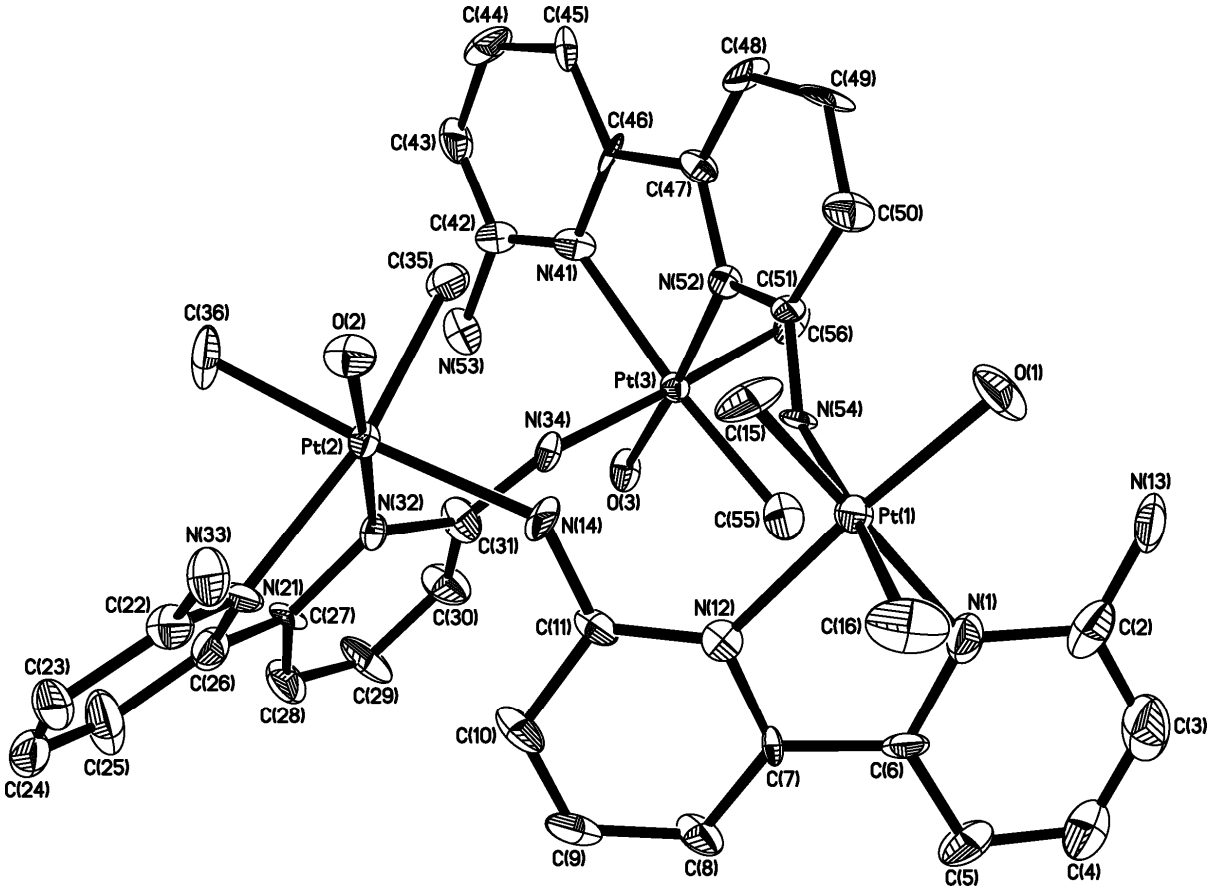

Fig. S14