Supplementary Information

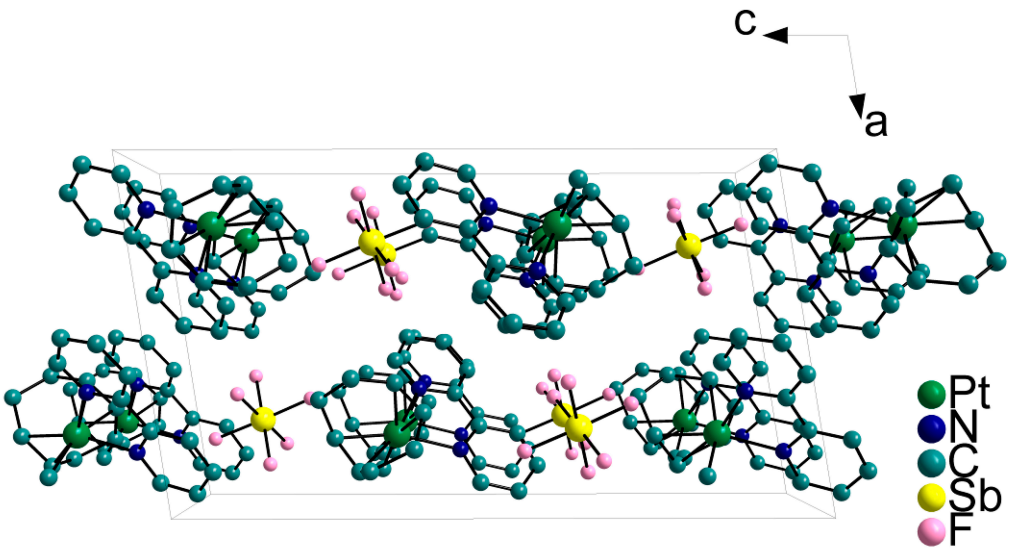


Figure S1. Crystal structure of [Pt(bpy)(cod)(Me)][SbF_6], viewed along the *b* axis.

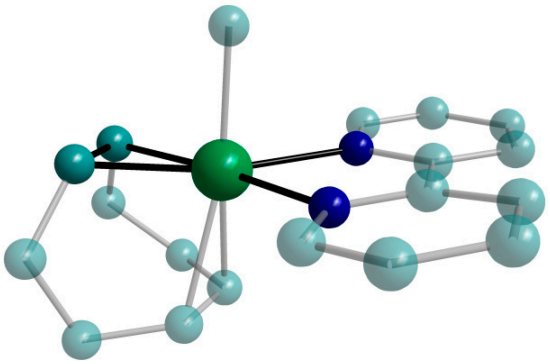


Figure S2. View of the molecular structure of [Pt(bpy)(cod)(Me)][SbF_6] at 50% probability level (with numbering); protons were omitted for clarity.

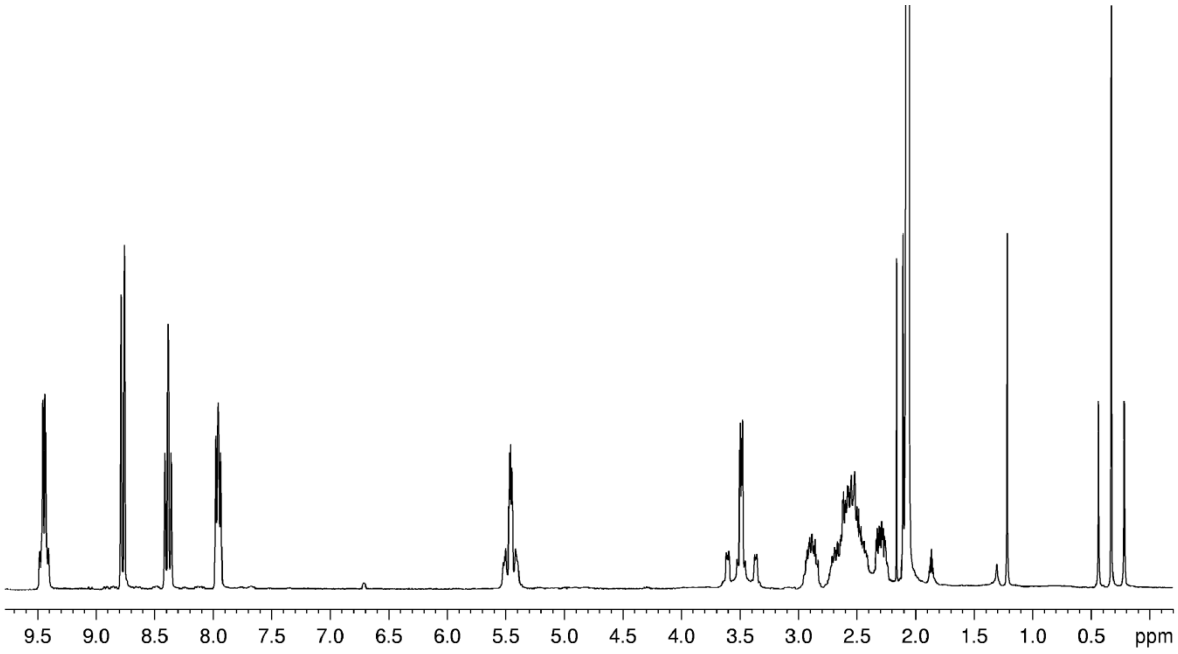


Figure S3. 300 MHz ^{1}H NMR spectrum of [Pt(bpy)(cod)(Me)][SbF_6] in acetone-d^6 at 298 K.

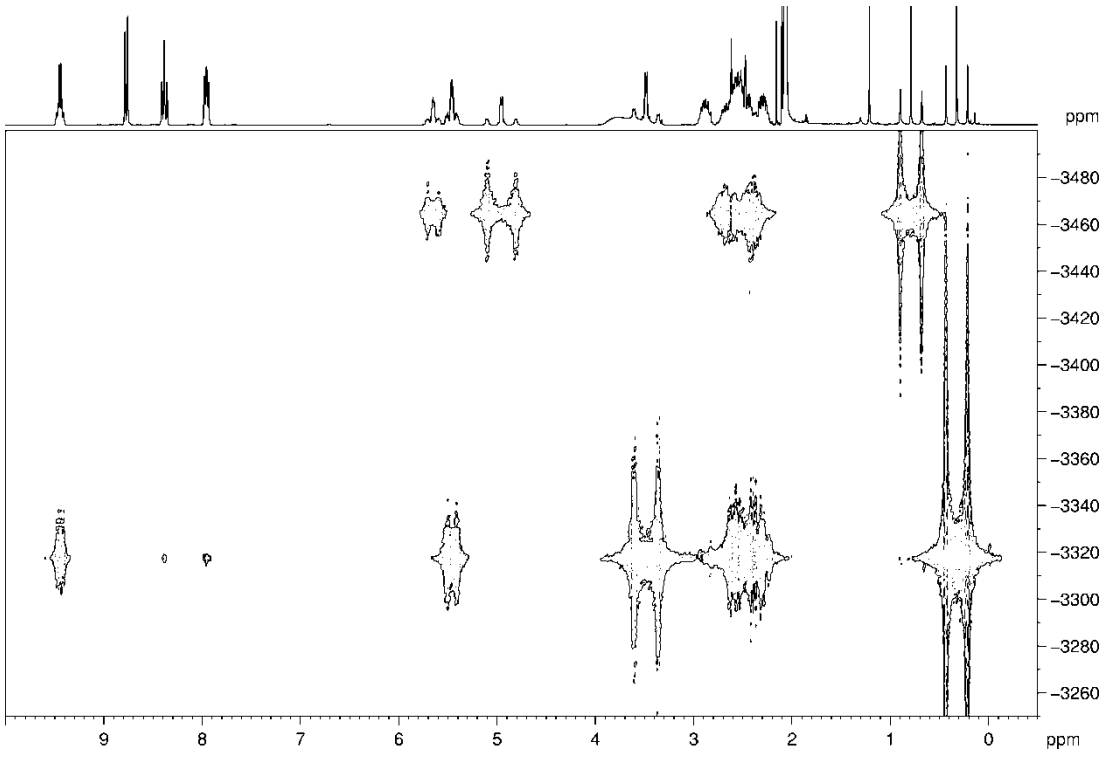


Figure S4. 300 MHz ^{1}H-^{195}Pt HMBC NMR spectra of a mixture of $[Pt(bpy)(cod)(Me)]^+$ (lower trace at δ^{195}Pt = –3318) and $[Pt(cod)(Me)(OH_2)]^+$ (upper trace at δ^{195}Pt = –3465) in acetone-d^6 at 298 K.

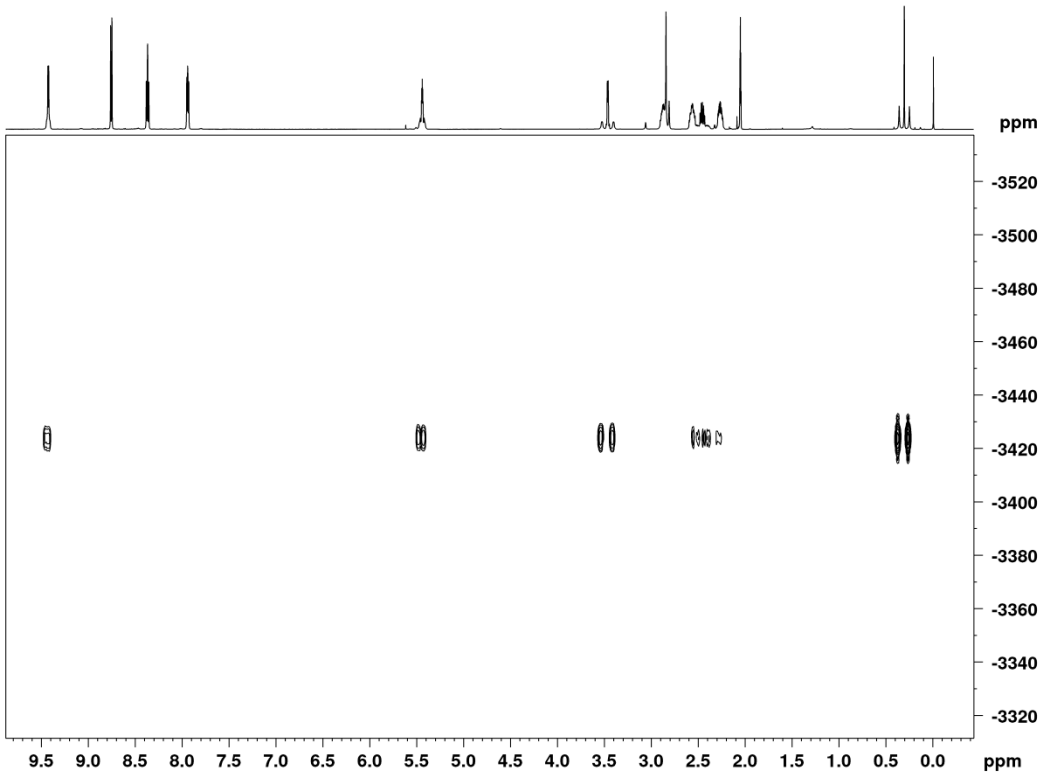


Figure S5. ^{1}H-^{195}Pt HMBC of [Pt(bpy)(cod)(Me)][SbF_6] in acetone-d^6 at 600 MHz and 298 K.

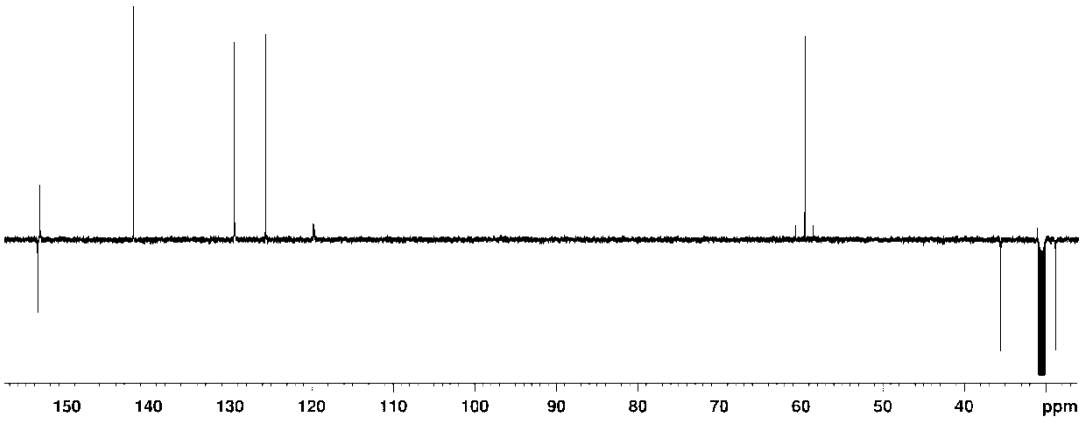


Figure S6. ^{13}C DEPTQ of [Pt(bpy)(cod)(Me)][SbF_6] in acetone-d^6 at 600 Mhz and 298 K.

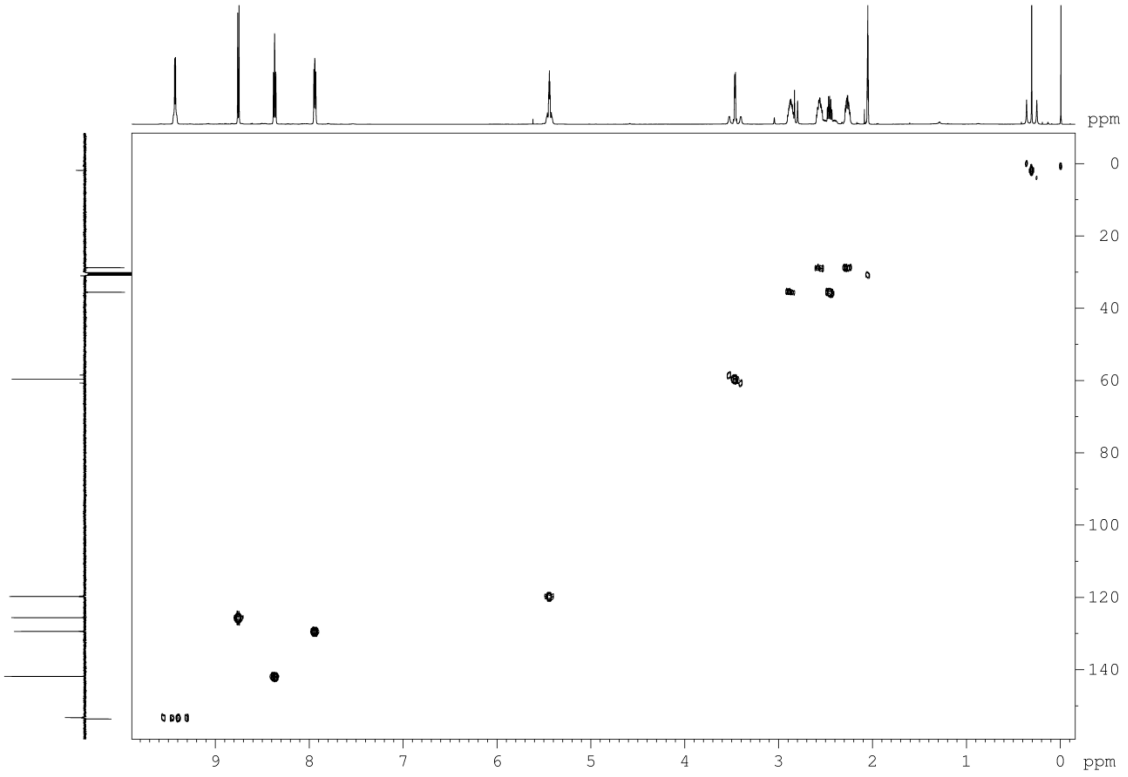


Figure S7. ^{1}H-^{13}C HMQC of [Pt(bpy)(cod)(Me)][SbF_6] in acetone-d^6 at 600 MHz and 298 K.

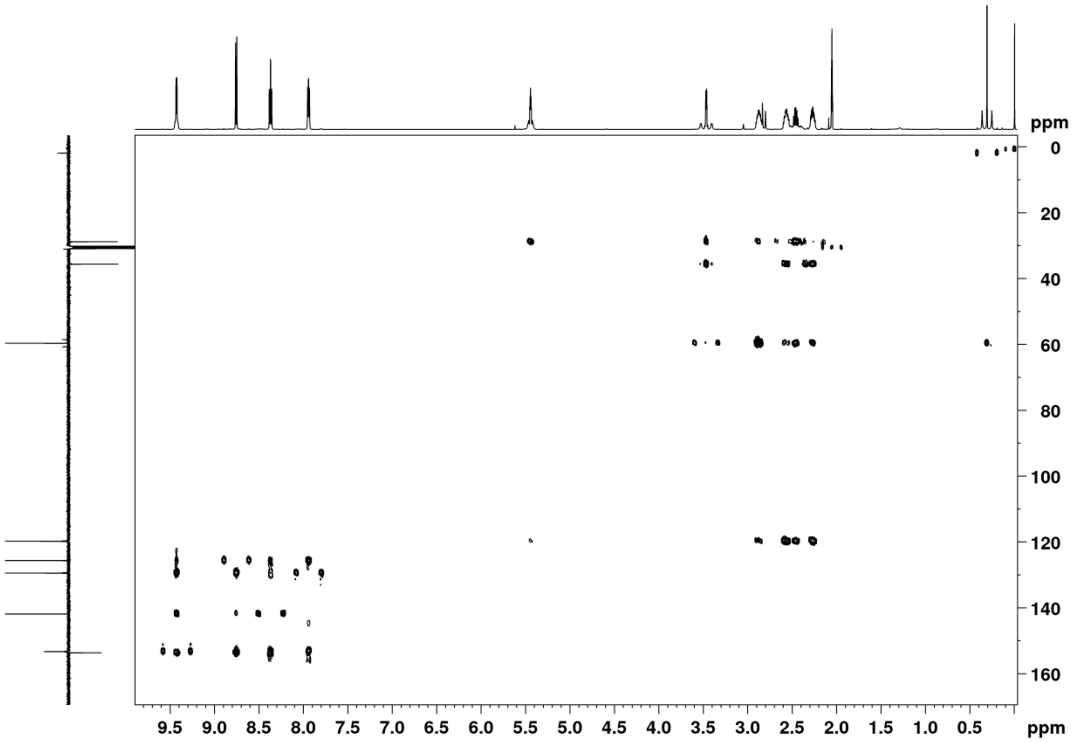


Figure S8. ^{1}H-^{13}C HMBC of [Pt(bpy)(cod)(Me)][SbF_6] in acetone-d^6 at 600 MHz and 298 K.

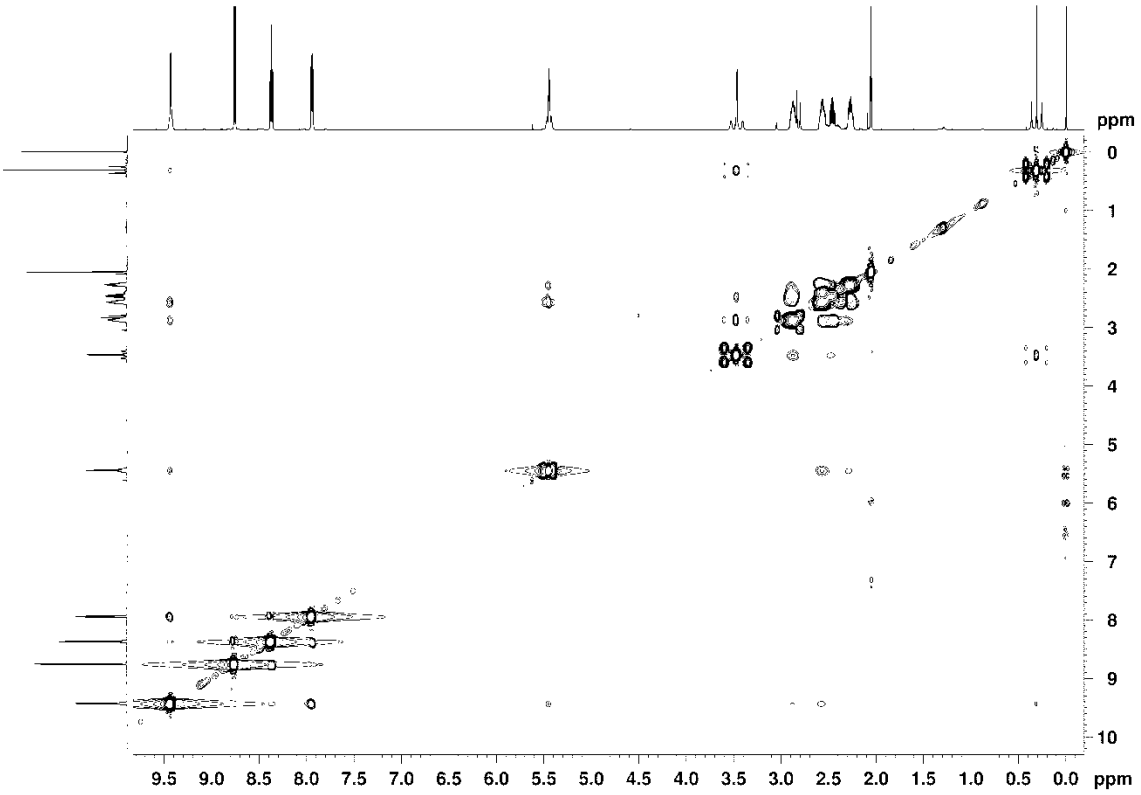
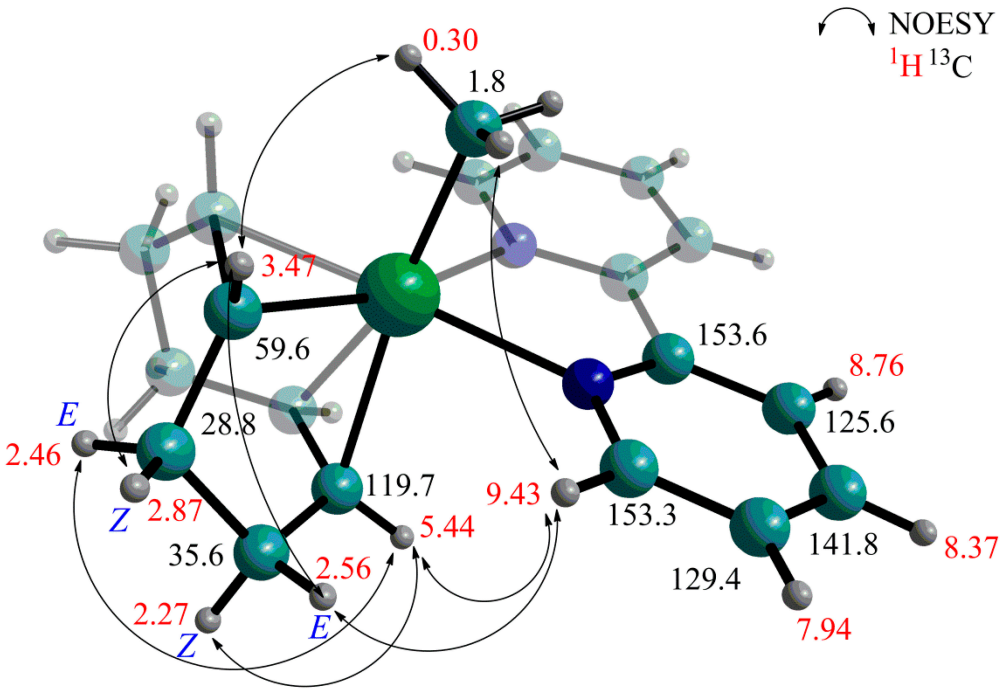


Figure S9. ^{1}H-^{1}H NOESY of [Pt(bpy)(cod)(Me)][SbF_6] in acetone-d^6 at 600 MHz and 298 K.



Scheme S1. Assignment of ^{1}H and ^{13}C signals and NOESY contacts (arrows) superimposed on the molecular structure of [Pt(bpy)(cod)(Me)]$^{+}$ from single crystal XRD.

Table S1. Crystal data and structure refinement for [Pt(bpy)(cod)(Me)][SbF_6].

CCDC	**1047002**
Empirical formula	C19 H23 F6 N2 Pt Sb
Formula weight	710.23
Temperature / Wavelength	293(2) K / 0.71073 Å
Crystal system / Space group	monoclinic / $P\ 2_1/c$
Unit cell dimensions	a = 11.8078(9) Å; b = 8.3564(7) Å; c = 21.0767(18) Å β = 99.052(6)°
Volume / Z	2053.8(3) $Å^3$ / 4
Density (calculated)	2.297 Mg/m^3
Absorption coefficient	8.180 mm^{-1}
F(000)	1336
Crystal size	0.2 x 0.2 x 0.1 mm^3
Theta range for data collection	1.746 to 27.418°.
Index ranges	$-15 < h < 13$, $-10 < k < 10$, $-26 < l < 26$
Reflections collected / independent	24266 / 4504 [R(int) = 0.1258]
Completeness to theta = 27.29°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4504 / 0 / 263
Goodness-of-fit on F^2	1.187
Final R indices [I>2sigma(I)]	$R_1 = 0.0644$, $wR_2 = 0.1613$
R indices (all data)	$R_1 = 0.0675$, $wR_2 = 0.1629$
Largest diff. peak and hole	4.279 and -3.242 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Pt(bpy)(cod)(Me)][SbF_6]. U(eq) is defined as one third of the trace of the orthogonalised U^{ij} tensor.

	x	**y**	**z**	**U(eq)**
Pt(1)	2186(1)	2550(1)	3551(1)	20(1)
N(20)	1722(8)	3182(13)	4501(5)	24(2)
N(10)	3419(7)	4412(12)	3982(4)	19(2)
C(25)	827(11)	2518(15)	4740(7)	31(3)
C(23)	1224(12)	4076(17)	5683(7)	36(3)
C(35)	2108(12)	1731(15)	2601(5)	27(3)
C(11)	3263(9)	5061(13)	4544(5)	21(2)
C(36)	1223(10)	932(14)	2926(6)	27(3)
C(12)	3914(9)	6382(14)	4802(6)	23(2)
C(41)	1106(10)	4438(15)	3199(6)	27(2)
C(33)	3793(11)	-45(17)	3041(7)	34(3)
C(22)	2111(10)	4788(15)	5453(6)	26(2)

Table S2. *Cont.*

	x	y	z	U(eq)
C(34)	3193(12)	954(18)	2474(6)	36(3)
C(31)	2862(10)	210(16)	4041(6)	29(3)
C(24)	554(11)	2942(18)	5316(7)	36(3)
C(37)	1333(11)	-799(15)	3131(6)	29(3)
C(38)	1921(12)	-998(16)	3841(7)	35(3)
C(13)	4754(10)	6983(15)	4470(6)	27(3)
C(15)	4225(10)	5006(15)	3663(6)	27(2)
C(14)	4907(10)	6292(16)	3897(6)	28(3)
C(21)	2351(9)	4303(13)	4850(5)	21(2)
C(32)	3662(10)	656(14)	3676(6)	26(2)
Sb(1)	2484(1)	5858(1)	1329(1)	26(1)
F(1)	1695(9)	7638(10)	1579(5)	50(2)
F(2)	3274(9)	4104(12)	1067(6)	65(3)
F(3)	3114(9)	5404(14)	2181(5)	62(3)
F(4)	1232(7)	4573(11)	1393(4)	45(2)
F(5)	1890(7)	6326(11)	468(4)	41(2)
F(6)	3736(7)	7195(11)	1257(5)	45(2)

Table S3. Bond lengths [Å] and angles [°] for [Pt(bpy)(cod)(Me)][SbF_6].

Pt(1)-C(41) 2.090(11)	**C(41)-Pt(1)-C(36) 91.4(5)**	**C(23)-C(22)-C(21) 118.2(12)**
Pt(1)-C(36) 2.093(10)	C(41)-Pt(1)-C(35) 88.5(5)	C(23)-C(22)-H(22) 120.9
Pt(1)-C(35) 2.105(10)	C(36)-Pt(1)-C(35) 41.7(5)	C(21)-C(22)-H(22) 120.9
Pt(1)-N(20) 2.222(10)	C(41)-Pt(1)-N(20) 85.3(4)	C(35)-C(34)-C(33) 113.6(11)
Pt(1)-N(10) 2.225(9)	C(36)-Pt(1)-N(20) 122.3(4)	C(35)-C(34)-H(34A) 108.9
Pt(1)-C(31) 2.295(12)	C(35)-Pt(1)-N(20) 162.8(4)	C(33)-C(34)-H(34A) 108.9
Pt(1)-C(32) 2.339(12)	C(41)-Pt(1)-N(10) 86.6(4)	C(35)-C(34)-H(34B) 108.9
N(20)-C(21) 1.341(14)	C(36)-Pt(1)-N(10) 164.6(4)	C(33)-C(34)-H(34B) 108.9
N(20)-C(25) 1.357(16)	C(35)-Pt(1)-N(10) 122.9(4)	H(34A)-C(34)-H(34B) 107.7
N(10)-C(11) 1.341(14)	N(20)-Pt(1)-N(10) 72.8(3)	C(32)-C(31)-C(38) 124.9(12)
N(10)-C(15) 1.345(15)	C(41)-Pt(1)-C(31) 162.3(5)	C(32)-C(31)-Pt(1) 74.7(7)
C(25)-C(24) 1.35(2)	C(36)-Pt(1)-C(31) 81.3(4)	C(38)-C(31)-Pt(1) 104.8(7)
C(25)-H(25) 0.9300	C(35)-Pt(1)-C(31) 96.4(5)	C(32)-C(31)-H(31) 114.7
C(23)-C(22) 1.359(18)	N(20)-Pt(1)-C(31) 85.1(4)	C(38)-C(31)-H(31) 114.7
C(23)-C(24) 1.39(2)	N(10)-Pt(1)-C(31) 104.7(4)	Pt(1)-C(31)-H(31) 114.7
C(23)-H(23) 0.9300	C(41)-Pt(1)-C(32) 162.4(5)	C(25)-C(24)-C(23) 118.9(12)
C(35)-C(36) 1.495(18)	C(36)-Pt(1)-C(32) 87.4(5)	C(25)-C(24)-H(24) 120.6
C(35)-C(34) 1.498(18)	C(35)-Pt(1)-C(32) 78.9(5)	C(23)-C(24)-H(24) 120.6
C(35)-H(35) 0.9800	N(20)-Pt(1)-C(32) 110.1(4)	C(36)-C(37)-C(38) 112.5(10)
C(11)-C(12) 1.405(15)	N(10)-Pt(1)-C(32) 89.9(4)	C(36)-C(37)-H(37A) 109.1
C(11)-C(21) 1.482(16)	C(31)-Pt(1)-C(32) 34.1(4)	C(38)-C(37)-H(37A) 109.1

Table S3. *Cont.*

C(36)-C(37) 1.509(17)	C(21)-N(20)-C(25) 118.7(11)	C(36)-C(37)-H(37B) 109.1
C(36)-H(36) 0.9800	C(21)-N(20)-Pt(1) 117.8(8)	C(38)-C(37)-H(37B) 109.1
C(12)-C(13) 1.393(17)	C(25)-N(20)-Pt(1) 123.6(8)	H(37A)-C(37)-H(37B) 107.8
C(12)-H(12) 0.9300	C(11)-N(10)-C(15) 119.9(10)	C(31)-C(38)-C(37) 113.2(11)
C(41)-H(41A) 0.9600	C(11)-N(10)-Pt(1) 118.1(7)	C(31)-C(38)-H(38A) 108.9
C(41)-H(41B) 0.9600	C(15)-N(10)-Pt(1) 121.6(8)	C(37)-C(38)-H(38A) 108.9
C(41)-H(41C) 0.9600	C(24)-C(25)-N(20) 122.3(12)	C(31)-C(38)-H(38B) 108.9
C(33)-C(32) 1.491(17)	C(24)-C(25)-H(25) 118.8	C(37)-C(38)-H(38B) 108.9
C(33)-C(34) 1.54(2)	N(20)-C(25)-H(25) 118.8	H(38A)-C(38)-H(38B) 107.8
C(33)-H(33A) 0.9700	C(22)-C(23)-C(24) 120.3(13)	C(14)-C(13)-C(12) 119.4(11)
C(33)-H(33B) 0.9700	C(22)-C(23)-H(23) 119.8	C(14)-C(13)-H(13) 120.3
C(22)-C(21) 1.406(16)	C(24)-C(23)-H(23) 119.8	C(12)-C(13)-H(13) 120.3
C(22)-H(22) 0.9300	C(36)-C(35)-C(34) 124.5(12)	N(10)-C(15)-C(14) 121.7(12)
C(34)-H(34A) 0.9700	C(36)-C(35)-Pt(1) 68.7(6)	N(10)-C(15)-H(15) 119.1
C(34)-H(34B) 0.9700	C(34)-C(35)-Pt(1) 113.6(8)	C(14)-C(15)-H(15) 119.1
C(31)-C(32) 1.360(18)	C(36)-C(35)-H(35) 113.9	C(13)-C(14)-C(15) 119.2(11)
C(31)-C(38) 1.511(18)	C(34)-C(35)-H(35) 113.9	C(13)-C(14)-H(14) 120.4
C(31)-H(31) 0.9800	Pt(1)-C(35)-H(35) 113.9	C(15)-C(14)-H(14) 120.4
C(24)-H(24) 0.9300	N(10)-C(11)-C(12) 121.1(11)	N(20)-C(21)-C(22) 121.6(11)
C(37)-C(38) 1.556(17)	N(10)-C(11)-C(21) 114.9(9)	N(20)-C(21)-C(11) 116.0(10)
C(37)-H(37A) 0.9700	C(12)-C(11)-C(21) 123.9(10)	C(22)-C(21)-C(11) 122.3(10)
C(37)-H(37B) 0.9700	C(35)-C(36)-C(37) 121.6(12)	C(31)-C(32)-C(33) 125.4(11)
C(38)-H(38A) 0.9700	C(35)-C(36)-Pt(1) 69.5(6)	C(31)-C(32)-Pt(1) 71.2(7)
C(38)-H(38B) 0.9700	C(37)-C(36)-Pt(1) 115.2(7)	C(33)-C(32)-Pt(1) 110.2(8)
C(13)-C(14) 1.377(18)	C(35)-C(36)-H(36) 114.3	C(31)-C(32)-H(32) 114.0
C(13)-H(13) 0.9300	C(37)-C(36)-H(36) 114.3	C(33)-C(32)-H(32) 114.0
C(15)-C(14) 1.386(17)	Pt(1)-C(36)-H(36) 114.3	Pt(1)-C(32)-H(32) 114.0
C(15)-H(15) 0.9300	C(13)-C(12)-C(11) 118.6(11)	F(4)-Sb(1)-F(2) 90.5(5)
C(14)-H(14) 0.9300	C(13)-C(12)-H(12) 120.7	F(4)-Sb(1)-F(3) 90.8(4)
C(32)-H(32) 0.9800	C(11)-C(12)-H(12) 120.7	F(2)-Sb(1)-F(3) 89.0(5)
Sb(1)-F(4) 1.848(8)	Pt(1)-C(41)-H(41A) 109.5	F(4)-Sb(1)-F(1) 90.1(4)
Sb(1)-F(2) 1.867(10)	Pt(1)-C(41)-H(41B) 109.5	F(2)-Sb(1)-F(1) 179.0(5)
Sb(1)-F(3) 1.871(9)	H(41A)-C(41)-H(41B) 109.5	F(3)-Sb(1)-F(1) 91.8(5)
Sb(1)-F(1) 1.874(9)	Pt(1)-C(41)-H(41C) 109.5	F(4)-Sb(1)-F(6) 178.9(4)

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for [Pt(bpy)(cod)(Me)][SbF_6]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U11	U22	U33	U23	U13	U12
Pt(1)	18(1)	24(1)	17(1)	1(1)	0(1)	-2(1)
N(20)	18(4)	33(5)	21(5)	-2(4)	7(4)	-3(4)
N(10)	12(4)	31(5)	15(4)	1(4)	6(3)	-5(4)
C(25)	22(6)	35(7)	34(7)	1(5)	2(5)	-11(5)
C(23)	39(7)	39(7)	34(7)	-4(6)	14(6)	-2(6)
C(35)	46(7)	32(6)	5(4)	-6(4)	9(5)	-4(5)
C(11)	20(5)	21(5)	21(5)	-4(4)	2(4)	1(4)
C(36)	28(6)	23(5)	24(6)	-1(5)	-12(5)	-14(5)
C(12)	19(5)	24(5)	26(6)	1(4)	6(4)	-1(4)
C(41)	21(5)	32(6)	27(6)	1(5)	1(5)	7(5)
C(33)	27(6)	39(7)	41(7)	-12(6)	22(6)	0(5)
C(22)	25(5)	35(6)	17(5)	1(5)	7(4)	-2(5)
C(34)	44(7)	42(7)	27(6)	-19(6)	21(6)	2(6)
C(31)	26(6)	34(6)	24(6)	6(5)	-8(5)	4(5)
C(24)	25(6)	48(8)	37(7)	15(6)	12(6)	-9(6)
C(37)	29(6)	27(6)	28(6)	-5(5)	-1(5)	-2(5)
C(38)	34(7)	32(7)	37(7)	-1(6)	2(6)	2(5)
C(13)	22(5)	27(6)	35(7)	4(5)	9(5)	-6(5)
C(15)	27(6)	32(6)	24(6)	4(5)	8(5)	-3(5)
C(14)	21(5)	37(7)	25(6)	5(5)	3(5)	-9(5)
C(21)	20(5)	24(5)	20(5)	-3(4)	2(4)	2(4)
C(32)	25(5)	27(6)	26(6)	-12(5)	8(5)	1(5)
Sb(1)	22(1)	32(1)	25(1)	6(1)	5(1)	4(1)
F(1)	57(6)	39(5)	54(6)	-15(4)	15(5)	4(4)
F(2)	60(6)	47(5)	91(8)	2(6)	22(6)	21(5)
F(3)	56(6)	89(8)	37(5)	26(5)	-8(4)	-7(6)
F(4)	38(4)	45(5)	51(5)	3(4)	8(4)	-11(4)
F(5)	43(4)	53(5)	27(4)	5(4)	2(4)	5(4)
F(6)	30(4)	53(5)	50(5)	20(4)	-3(4)	-8(4)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Pt(bpy)(cod)(Me)][SbF_6].

	x	y	z	U(eq)
H(25)	387	1744	4498	37
H(23)	1065	4348	6087	44
H(35)	1793	2515	2274	33
H(36)	435	1277	2772	32
H(12)	3787	6845	5185	27
H(41A)	1369	5408	3418	41
H(41B)	339	4211	3270	41
H(41C)	1114	4562	2747	41
H(33A)	3476	-1118	3012	40
H(33B)	4603	-125	3012	40
H(22)	2548	5576	5689	31
H(34A)	3717	1777	2374	43
H(34B)	3019	267	2101	43
H(31)	3112	293	4505	35
H(24)	-72	2482	5465	43
H(37A)	1777	-1367	2853	34
H(37B)	576	-1278	3079	34
H(38A)	1345	-892	4120	42
H(38B)	2241	-2066	3898	42
H(13)	5206	7844	4634	33
H(15)	4329	4542	3275	33
H(14)	5462	6683	3669	33
H(32)	4381	1040	3926	31