Using Reduced Catalysts for Oxidation Reactions: Mechanistic Studies of the "Periana-Catalytica" System for CH_4 Oxidation.

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1 General Procedures

Unless otherwise noted, all reactions were carried out under an inert atmosphere of nitrogen or argon utilizing standard Schlenk glassware techniques or a Vacuum Atmospheres drybox. Elemental analyses were carried out by Desert Analytics Laboratory, Tucson, AZ. ^{1}H, ^{13}C and ^{19}F NMR spectra were collected using Bruker AC-250 (^{1}H at 250.134 MHz and ^{13}C at 62.902 MHz), AM-360 (^{1}H at 360.138 MHz and ^{13}C at 90.566 MHz), and Varian Mercury 400 spectrometers (^{1}H at 400.151 MHz and ^{13}C at 100.631 MHz). The spectra were referenced to residual solvent protons or a known chemical shift standard and chemical shifts are reported in parts per million downfield of tetramethylsilane. All coupling constants are reported in Hertz. NMR experiments requiring air-free manipulations were carried out in Wilmad NMR tubes fitted with J. Young Teflon vacuum/pressure valves. Liquid and gas phases of reaction products were analyzed on Shimadzu QP-5000 GCMS instrument. Gas phases were analyzed using a J&W Scientific GasPro capillary column (30 m × 0.32 mm ID), liquid phase on J&W Scientific DS-5ms capillary column (30 m × 0.32 mm ID). Unless otherwise noted, reagent grade chemicals were purchased from commercial suppliers and used without further purification. Hydrocarbon solvents, ether, and THF were distilled from sodium/benzophenone under argon; inhibitor-free dry dichloromethane was obtained via standard procedures and finally purified by careful distillation from CaH_2 immediately prior to use. Deuterated solvents for NMR experiments were purified by identical procedures. SO_2 was distilled from P_2O_5 directly into an NMR tube immediately prior to use except during reactions on larger scale (described separately below).

Catalytic methane oxidation experiments were carried out as described in the original procedures.[1] For NMR analysis, a known amount of acetic acid was added to an aliquot of the reaction solution as an internal standard. Methyl bisulfate (and any free methanol) was determined from the ratio of the ^{1}H NMR methyl resonances of methyl bisulfate (3.4 ppm) to acetic acid (2.02 ppm). The methyl products were also quantified by HPLC analysis of the liquid phase. Known volume aliquots of reaction solution were first hydrolyzed by the addition of 3 parts water to 1 part crude reaction solution and heated to 90 °C for 4 h in a sealed vial. The hydrolyzed solution was analyzed using a HP 1050 HPLC equipped with a HPX-87H column (Bio-Rad) and a refractive index detector. The eluent was 0.1 volume % sulfuric acid in water. Methanol eluted at 16.2 minutes. The gas phase (CH_4, CO_2 and CH_3Cl) and liquid phase (CH_3OSO_3H and CH_3OH) analyses allowed >90% mass balance on methane.

2 Procedures

Stir Rate Dependence on H/D Exchange of CH_4: In a 25 mL Hast C autoclave with a glass liner and overhead stirrer, a 2.5 mM solution of Pt(bpym)Cl_2 in 98% D_2SO_4 was prepared and charged with methane following several purge cycles. The reactor was heated at 165 °C for 40 min with stirring rates from 0-1200 RPM. The gas phase was then analyzed by venting a portion of the head space into a septum capped, evacuated vial, which was followed by GC-MS analysis of the methane isotoplogues. Analysis demonstrated that no increase in rate was observed above a stir rate of 200 rpm; indicating that above this stir rate mass transport was not an issue (Figure S1).

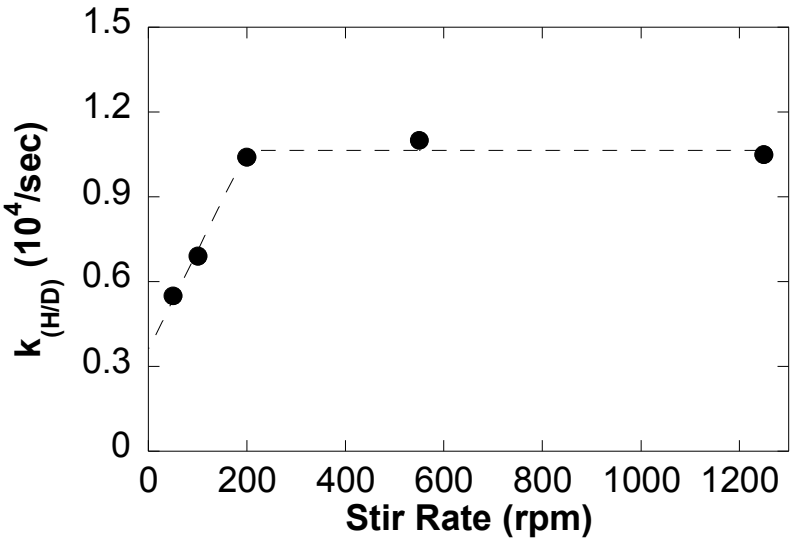

Figure S1. Plot of observed H/D exchange rate vs. agitation speed, where [Pt(bpym)Cl_2] = 2.5 mM at 165 °C for 40 min.

Methane Pressure Dependence on H/D Exchange of CH_4: A stainless steel autoclave with a glass liner and magnetic stir bar was charged with a 5 mM solution of Pt(bpym)Cl_2 in 98% D_2SO_4. The reactor was pressurized with methane following several purge cycles. The reactor was then heated at 165 °C for 40 min. The gas phase was then analyzed by venting a portion of the head space into a septum capped, evacuated vial, which was followed by GC-MS analysis of the methane isotoplogues.

Activation Parameters for H/D Exchange and Oxidation of CH_4: A stainless steel autoclave with a glass liner and magnetic stir bar was charged with a 35 mM solution of Pt(bpym)Cl_2 in concentrated sulfuric acid (D_2SO_4 for H/D exchange and H_2SO_4 for oxidation reactions, respectively). The reactor was pressurized with methane following several purge cycles. The reactor was then heated at 169-190 °C for 40 min. The reaction was then analyzed by

gas phase GC-MS and liquid phase HPLC and NMR analysis as described in the general procedures.

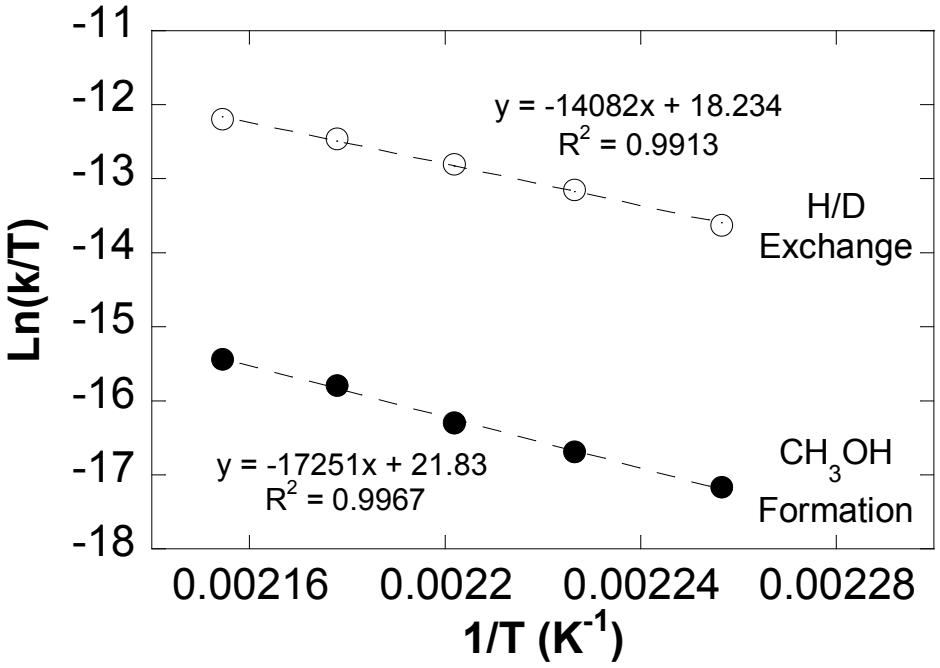

Figure S2. Eyring plot for the Pt(bpym)Cl_2 catalyzed H/D exchange of CH_4 (○) and oxidation of CH_4 (●) in D_2SO_4, where [Pt(bpym)Cl_2] = 35 mM from 169-190 °C. H/D Exchange: $\Delta H^{\ddagger}$ = 28.0 ± 2.4 kcal/mol, $\Delta S^{\ddagger}$ = -11.0 ± 3.3 eu; CH_3OH Formation: $\Delta H^{\ddagger}$ = 34.3 ± 2.1 kcal/mol, $\Delta S^{\ddagger}$ = -3.8 ± 0.8 eu.

Reaction Rate as a Function of Solvent Acidity: A stainless steel autoclave with a glass liner and magnetic stir bar was charged with a 2.5 mM solution of Pt(bpym)Cl_2 in 85-98 wt% D_2SO_4 in D_2O. The reactor was pressurized with methane following several purge cycles. The reactor was then heated at 150 °C for 40 min. The reaction was then analyzed by gas phase GC-MS.

Comparison of Methane Deuteration from Pt-Me Intermediate to Catalytic Reaction: A solution of Pt(bpym)(CH_3)(X) (where X = Cl or $OCOCF_3$) in HOAc-D_4 was added to D_2SO_4 at

room temperature or 180 °C followed to generate a final concentration of 10 mM Pt(bpym). Analysis of the headspace following the reaction, followed by subsequent GC-MS analysis of the methane was performed.

Table S1. Ratio of deuteromethanes (d_1:d_2:d_3:d_4) from direct catalytic reaction with CH_4 and from reverse reaction of Pt^{II}-CH_3 deuterolysis.

	% of Methane Isotopologues			
	CH_3D	CH_2D_2	CHD_3	CD_4
Catalytic Runs	48	38	10	4
Pt^{II}-CH_3 deuterolysis	46	33	14	5

3 Arrhenius calculation from $\Delta G^{\ddagger}$

Scheme S1. Arrhenius calculation of TOF from $\Delta G^{\ddagger}$

$$k = \frac{k_B T}{h} e^{-\left(\frac{\Delta G^{\ddagger}}{RT}\right)}$$

$$k = \frac{(1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}}) * (493.15\mathrm{K})}{6.626 \times 10^{-34}\ \mathrm{J\ s}} e^{-\left(\frac{(41\ \mathrm{kcal\ mol^{-1}}) * (4184\ \mathrm{J\ kcal^{-1}})}{(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) * (493.15\mathrm{K})}\right)}$$

$$k = (1.0278 \times 10^{13}\ \mathrm{s^{-1}}) * e(-41.839)$$

$$k = 6.94 \times 10^{-6}$$

4 X-Ray Data

X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The cell parameters were obtained from a least-squares refinement of the spots using the program SMART. A hemisphere of data was collected up to a resolution of 0.75 Å. The intensity data were processed using the program Saint-Plus. All calculations for the structure determination were carried out using the SHELXTL package (version 5.1).[2] Initial atomic coordinates of the Pt atoms were located by direct methods, and structures were refined by least-squares methods. Empirical absorption corrections were applied using the program SADABS.[3] Calculated hydrogen positions were input and refined in a riding manner along with their attached carbons. A summary of the refinement details and the resulting parameters are given in the Supporting Information. Ortep-3 for Windows[4] was used for plotting the structures for publication.

Figure S3. Ortep drawing of Pt(bpym)Cl4·0.5DMF with DMF and hydrogens omitted for clarity.

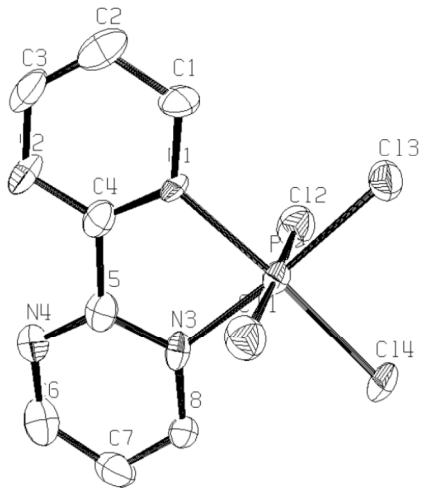

Table S2. Crystal data and structure refinement for $Pt(bpym)Cl_4 \cdot 0.5DMF$.

Identification code	ptcl4m
Empirical formula	C9.50 H9 Cl4 N4.50 O Pt
Formula weight	539.10
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbcn
Unit cell dimensions	a = 17.908(5) Å α= 90°.
	b = 13.152(3) Å β= 90°.
	c = 12.165(3) Å γ = 90°.
Volume	2865.3(12) Å3
Z	8
Density (calculated)	2.499 Mg/m^3
Absorption coefficient	10.539 mm^{-1}
F(000)	2012
Crystal size	0.15 x 0.15 x 0.02 mm^3
Theta range for data collection	1.92 to 27.48°.
Index ranges	-22<=h<=23, -16<=k<=17, -11<=l<=15
Reflections collected	16230
Independent reflections	3258 [R(int) = 0.0668]
Completeness to theta = 27.48°	99.1 %
Transmission factors min/max ratio:	0.481
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3258 / 0 / 178
Goodness-of-fit on F^2	1.037102
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1051
R indices (all data)	R1 = 0.0715, wR2 = 0.1138
Largest diff. peak and hole	1.836 and -1.378 $e.Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for Pt(bpym)Cl4·0.5DMF. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pt(1)	1866(1)	1527(1)	1483(1)	25(1)
Cl(1)	3017(1)	2109(2)	2067(2)	41(1)
Cl(2)	672(1)	990(2)	1012(2)	42(1)
Cl(3)	2294(1)	1289(2)	-279(2)	34(1)
Cl(4)	2215(1)	-105(2)	1906(2)	36(1)
C(1)	1489(6)	3490(6)	262(7)	38(2)
C(2)	1147(5)	4445(7)	237(9)	44(3)
C(3)	849(6)	4820(7)	1186(9)	45(3)
C(4)	1159(5)	3400(6)	2096(7)	30(2)
C(5)	1151(5)	2763(6)	3118(7)	29(2)
C(6)	841(5)	2504(7)	4869(9)	45(3)
C(7)	1183(6)	1549(7)	4854(8)	41(2)
C(8)	1489(5)	1239(6)	3897(7)	30(2)
C(9)	513(7)	1264(11)	8148(11)	77(4)
N(5)	0	1809(11)	7500	56(3)
C(10)	0	2890(20)	7500	94(7)
O(1)	343(13)	3336(17)	8189(18)	220(10)
N(1)	1482(4)	2977(5)	1227(5)	23(2)
N(2)	848(4)	4318(5)	2130(6)	36(2)
N(3)	1477(4)	1852(5)	3007(6)	27(2)
N(4)	823(4)	3118(6)	4008(6)	33(2)

Table S4. Bond lengths [Å] and angles [°] for Pt(bpym)Cl4·0.5DMF.

Pt(1)-N(3)	2.026(7)
Pt(1)-N(1)	2.052(6)
Pt(1)-Cl(4)	2.293(2)
Pt(1)-Cl(3)	2.298(2)
Pt(1)-Cl(1)	2.309(2)
Pt(1)-Cl(2)	2.324(3)
C(1)-N(1)	1.353(10)
C(1)-C(2)	1.398(12)
C(2)-C(3)	1.364(14)
C(3)-N(2)	1.325(12)
C(4)-N(1)	1.327(11)
C(4)-N(2)	1.330(10)
C(4)-C(5)	1.499(12)
C(5)-N(4)	1.318(11)
C(5)-N(3)	1.340(10)
C(6)-N(4)	1.322(12)
C(6)-C(7)	1.398(13)
C(7)-C(8)	1.349(13)
C(8)-N(3)	1.350(11)
C(9)-N(5)	1.408(14)
N(5)-C(9)	1.408(14)
N(5)-C(10)	1.42(3)
C(10)-O(1)	1.19(2)
C(10)-O(1)	1.19(2)
N(3)-Pt(1)-N(1)	80.1(3)
N(3)-Pt(1)-Cl(4)	94.9(2)
N(1)-Pt(1)-Cl(4)	174.50(19)
N(3)-Pt(1)-Cl(3)	175.6(2)

N(1)-Pt(1)-Cl(3)	95.55(18)
Cl(4)-Pt(1)-Cl(3)	89.47(8)
N(3)-Pt(1)-Cl(1)	87.4(2)
N(1)-Pt(1)-Cl(1)	92.2(2)
Cl(4)-Pt(1)-Cl(1)	89.90(9)
Cl(3)-Pt(1)-Cl(1)	91.99(8)
N(3)-Pt(1)-Cl(2)	88.5(2)
N(1)-Pt(1)-Cl(2)	86.3(2)
Cl(4)-Pt(1)-Cl(2)	91.25(9)
Cl(3)-Pt(1)-Cl(2)	92.04(9)
Cl(1)-Pt(1)-Cl(2)	175.82(9)
N(1)-C(1)-C(2)	117.5(9)
C(3)-C(2)-C(1)	118.6(9)
N(2)-C(3)-C(2)	123.6(8)
N(1)-C(4)-N(2)	126.0(8)
N(1)-C(4)-C(5)	115.5(7)
N(2)-C(4)-C(5)	118.5(8)
N(4)-C(5)-N(3)	126.4(8)
N(4)-C(5)-C(4)	119.3(8)
N(3)-C(5)-C(4)	114.4(7)
N(4)-C(6)-C(7)	123.3(9)
C(8)-C(7)-C(6)	117.4(9)
C(7)-C(8)-N(3)	120.4(8)
C(9)#1-N(5)-C(9)	118.7(17)
C(9)#1-N(5)-C(10)	120.6(9)
C(9)-N(5)-C(10)	120.6(9)
O(1)-C(10)-O(1)#1	121(3)
O(1)-C(10)-N(5)	119.3(17)
O(1)#1-C(10)-N(5)	119.3(17)
C(4)-N(1)-C(1)	119.1(7)

C(4)-N(1)-Pt(1)	114.5(5)
C(1)-N(1)-Pt(1)	126.3(6)
C(3)-N(2)-C(4)	115.2(8)
C(5)-N(3)-C(8)	117.4(7)
C(5)-N(3)-Pt(1)	115.5(6)
C(8)-N(3)-Pt(1)	127.1(6)
C(5)-N(4)-C(6)	115.1(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+3/2

Table S5. Anisotropic displacement parameters ($Å^2$x 10^3) for Pt(bpym)Cl_4·0.5DMF. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h2 a*2U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pt(1)	33(1)	16(1)	28(1)	-1(1)	0(1)	1(1)
Cl(1)	45(2)	36(1)	41(1)	-3(1)	2(1)	-5(1)
Cl(2)	43(1)	34(1)	49(1)	-3(1)	-3(1)	-2(1)
Cl(3)	44(1)	27(1)	32(1)	-5(1)	3(1)	-1(1)
Cl(4)	48(1)	17(1)	44(1)	0(1)	1(1)	9(1)
C(1)	58(6)	26(5)	29(5)	10(4)	-1(4)	-8(4)
C(2)	38(6)	31(5)	64(7)	19(5)	-2(5)	-7(4)
C(3)	56(7)	17(4)	62(7)	5(4)	-4(5)	6(4)
C(4)	29(5)	21(4)	39(5)	-1(4)	-3(4)	-2(4)
C(5)	27(5)	22(4)	40(5)	-4(4)	-1(4)	-9(4)
C(6)	47(6)	41(6)	48(6)	-13(5)	5(5)	-6(5)
C(7)	56(7)	40(5)	26(5)	3(4)	-5(4)	-11(5)
C(8)	44(6)	18(4)	29(5)	-2(3)	-8(4)	1(4)
C(9)	75(10)	89(11)	66(9)	0(7)	18(7)	9(8)
N(5)	55(9)	66(9)	46(8)	0	7(7)	0
C(10)	120(20)	109(19)	57(13)	0	52(13)	0
N(1)	34(4)	10(3)	26(4)	4(3)	-3(3)	2(3)
N(2)	39(5)	17(4)	53(5)	5(3)	6(4)	7(3)
N(3)	29(4)	16(3)	36(4)	-8(3)	2(3)	-2(3)
N(4)	34(5)	31(4)	33(4)	-6(4)	3(3)	1(3)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for Pt(bpym)Cl_4·0.5DMF.

	x	y	z	U(eq)
H(1)	1718	3211	-374	45
H(2)	1122	4824	-426	53
H(3)	630	5478	1169	54
H(6)	610	2724	5530	54
H(7)	1199	1134	5493	49
H(8)	1713	586	3850	36
H(9A)	814	1741	8581	115
H(9B)	841	863	7671	115
H(9C)	242	808	8645	115

Figure S4. ORTEP drawing of $Pt(bpym)(CH_3)(OCOCF_3)$ with CH_2Cl_2 and hydrogens omitted for clarity.

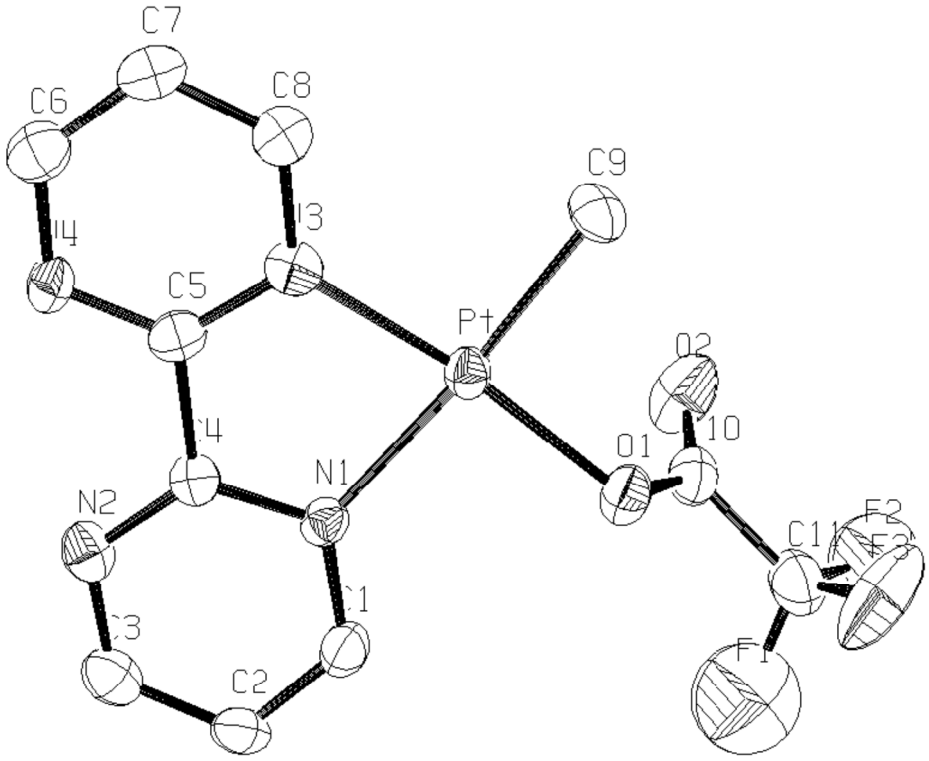

Table S7. Crystal data and structure refinement for Pt(bpym)(CH_3)($OCOCF_3$)·CH2Cl2.

Identification code	bpmptmem
Empirical formula	C12 H11 Cl2 F3 N4 O2 Pt
Formula weight	566.24
Temperature	143(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 8.9805(13) Å α= 90°.
	b = 23.393(3) Å β= 96.713(2)°.
	c = 7.7775(11) Å γ = 90°.
Volume	1622.7(4) $Å^3$
Z	4
Density (calculated)	2.318 Mg/m^3
Absorption coefficient	9.022 mm^{-1}
F(000)	1064
Crystal size	0.14 x 0.13 x 0.01 mm^3
Theta range for data collection	2.28 to 27.48°.
Index ranges	-11<=h<=11, -29<=k<=15, -9<=l<=10
Reflections collected	9838
Independent reflections	3619 [R(int) = 0.0444]
Completeness to theta = 27.48°	97.2 %
Transmission factors min/max ratio:	0.584
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3619 / 0 / 208
Goodness-of-fit on F_2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.0947
R indices (all data)	R1 = 0.0547, wR2 = 0.1005
Largest diff. peak and hole	2.030 and -1.260 e.$Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Pt(bpym)(CH_3)($OCOCF_3$)·CH_2Cl_2. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pt(1)	3932(1)	7887(1)	6790(1)	25(1)
Cl(1)	8403(3)	9544(1)	8323(3)	54(1)
Cl(2)	10063(3)	8980(1)	11292(3)	49(1)
F(1)	3919(11)	9891(5)	6197(13)	133(3)
F(2)	1564(9)	9946(4)	5767(10)	96(2)
F(3)	2613(9)	9745(3)	8215(8)	85(2)
O(1)	3624(6)	8737(2)	7066(6)	33(1)
O(2)	1687(8)	8845(3)	4987(8)	56(2)
N(1)	5959(7)	7996(2)	5769(8)	24(1)
N(2)	7835(7)	7452(3)	4592(8)	31(2)
N(3)	4482(7)	7069(3)	6490(7)	27(1)
N(4)	6252(7)	6473(3)	5306(8)	29(1)
C(1)	6718(9)	8480(3)	5512(10)	31(2)
C(2)	8041(8)	8472(4)	4803(10)	33(2)
C(3)	8566(9)	7936(4)	4348(10)	36(2)
C(4)	6584(8)	7500(3)	5314(9)	25(2)
C(5)	5722(8)	6979(3)	5704(9)	27(2)
C(6)	5468(9)	6022(4)	5744(10)	37(2)
C(7)	4204(9)	6068(4)	6552(10)	37(2)
C(8)	3729(9)	6609(4)	6922(9)	32(2)
C(9)	1963(9)	7722(4)	7705(10)	32(2)
C(10)	2617(9)	9012(3)	6113(10)	33(2)
C(11)	2687(10)	9645(4)	6567(13)	47(2)
C(12)	9371(10)	8929(3)	9079(10)	38(2)

Table S9. Bond lengths [Å] and angles [°] for Pt(bpym)(CH_3)($OCOCF_3$)·CH_2Cl_2.

Pt(1)-N(3)	1.996(6)
Pt(1)-C(9)	2.019(7)
Pt(1)-O(1)	2.022(5)
Pt(1)-N(1)	2.085(6)
Cl(1)-C(12)	1.748(9)
Cl(2)-C(12)	1.764(8)
F(1)-C(11)	1.309(12)
F(2)-C(11)	1.325(11)
F(3)-C(11)	1.312(11)
O(1)-C(10)	1.274(9)
O(2)-C(10)	1.203(10)
N(1)-C(1)	1.348(9)
N(1)-C(4)	1.354(9)
N(2)-C(4)	1.319(9)
N(2)-C(3)	1.333(10)
N(3)-C(8)	1.334(10)
N(3)-C(5)	1.348(10)
N(4)-C(5)	1.326(9)
N(4)-C(6)	1.335(10)
C(1)-C(2)	1.367(10)
C(2)-C(3)	1.400(11)
C(4)-C(5)	1.493(10)
C(6)-C(7)	1.365(11)
C(7)-C(8)	1.378(12)
C(10)-C(11)	1.522(12)
N(3)-Pt(1)-C(9)	95.5(3)
N(3)-Pt(1)-O(1)	173.4(2)
C(9)-Pt(1)-O(1)	90.8(3)

N(3)-Pt(1)-N(1)	80.4(2)
C(9)-Pt(1)-N(1)	175.7(3)
O(1)-Pt(1)-N(1)	93.3(2)
C(10)-O(1)-Pt(1)	122.1(5)
C(1)-N(1)-C(4)	116.7(6)
C(1)-N(1)-Pt(1)	129.6(5)
C(4)-N(1)-Pt(1)	113.7(5)
C(4)-N(2)-C(3)	116.6(7)
C(8)-N(3)-C(5)	117.3(7)
C(8)-N(3)-Pt(1)	127.1(6)
C(5)-N(3)-Pt(1)	115.5(5)
C(5)-N(4)-C(6)	115.6(7)
N(1)-C(1)-C(2)	121.8(7)
C(1)-C(2)-C(3)	116.7(7)
N(2)-C(3)-C(2)	122.6(7)
N(2)-C(4)-N(1)	125.7(7)
N(2)-C(4)-C(5)	120.3(7)
N(1)-C(4)-C(5)	113.9(7)
N(4)-C(5)-N(3)	125.7(7)
N(4)-C(5)-C(4)	118.1(7)
N(3)-C(5)-C(4)	116.1(7)
N(4)-C(6)-C(7)	123.2(8)
C(6)-C(7)-C(8)	117.6(8)
N(3)-C(8)-C(7)	120.7(7)
O(2)-C(10)-O(1)	130.2(8)
O(2)-C(10)-C(11)	119.4(8)
O(1)-C(10)-C(11)	110.4(7)
F(1)-C(11)-F(3)	106.1(9)
F(1)-C(11)-F(2)	106.2(9)
F(3)-C(11)-F(2)	104.0(8)

F(1)-C(11)-C(10)	113.0(9)
F(3)-C(11)-C(10)	113.3(8)
F(2)-C(11)-C(10)	113.6(9)
Cl(1)-C(12)-Cl(2)	112.1(5)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2$ x 10^3) for $Pt(bpym)(CH_3)(OCOCF_3)\cdot CH_2Cl_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h2\ a^*2U11 + ... + 2\ h\ k\ a^*\ b^*\ U12]$

	U11	U22	U33	U23	U13	U12
Pt(1)	25(1)	26(1)	23(1)	-2(1)	2(1)	3(1)
Cl(1)	76(2)	36(1)	48(1)	7(1)	0(1)	-2(1)
Cl(2)	44(1)	49(1)	52(1)	6(1)	-2(1)	-5(1)
F(3)	156(7)	46(4)	51(4)	-18(3)	4(4)	12(4)
O(1)	35(3)	31(3)	33(3)	-7(2)	0(2)	6(2)
O(2)	66(4)	43(4)	51(4)	-6(3)	-19(3)	15(3)
N(1)	25(3)	21(3)	26(3)	1(2)	0(2)	2(2)
N(2)	30(3)	40(4)	23(3)	-2(3)	4(3)	4(3)
N(3)	30(3)	30(4)	21(3)	6(3)	1(2)	0(3)
N(4)	30(3)	23(3)	35(3)	2(3)	4(3)	6(3)
C(1)	33(4)	27(4)	34(4)	-7(3)	1(3)	3(3)
C(2)	28(4)	38(5)	33(4)	-4(4)	3(3)	-10(4)
C(3)	29(4)	46(5)	32(4)	-1(4)	2(3)	-2(4)
C(4)	26(4)	26(4)	21(3)	4(3)	0(3)	3(3)
C(5)	31(4)	28(4)	21(3)	-2(3)	-2(3)	-4(3)
C(6)	42(5)	33(5)	35(4)	3(4)	1(4)	-1(4)
C(7)	43(5)	30(5)	38(4)	1(4)	3(4)	-8(4)
C(8)	36(4)	33(5)	24(4)	3(3)	2(3)	0(4)
C(9)	32(4)	35(4)	32(4)	11(3)	13(3)	2(3)
C(10)	37(4)	30(4)	34(4)	3(3)	10(4)	5(4)
C(11)	38(5)	41(5)	65(6)	5(5)	16(4)	8(4)
C(12)	52(5)	31(5)	35(4)	-1(4)	16(4)	-8(4)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Pt(bpym)(CH_3)($OCOCF_3$)·CH_2Cl_2.

	x	y	z	U(eq)
H(1)	6322	8836	5831	38
H(2)	8578	8813	4628	40
H(3)	9479	7916	3845	43
H(6)	5806	5651	5479	44
H(7)	3671	5738	6850	45
H(8)	2856	6656	7490	38
H(9A)	1258	7557	6780	49
H(9B)	1547	8078	8112	49
H(9C)	2127	7450	8669	49
H(12A)	10219	8864	8396	46
H(12B)	8691	8595	8905	46

5 Computational Details

5.1 Methodology

All calculations were performed with the hybrid density functional B3LYP[5] as implemented in Jaguar 7.0.[6] Geometry optimizations included solvation using the Poisson-Boltzmann reactive field (PBF)[7] with a dielectric constant of 98.0 and a probe radius of 2.205 to simulate sulfuric acid.[8] For solvation of smaller ions two explicit solvent molecules were included. For geometry optimizations the smaller LACVP** basis set[9] augmented with an extra d-function on sulfur. For single point energies we used the LACV3P**++ basis set augmented with one f-function on platinum and two d-functions and an f-function on sulfur.[10] Frequency calculations were performed numerically including the PBF-solver at the B3LYP/LACVP**(+d on S) level.

Free energies were calculated as the sum G = E(lacv3p**++ 2df(S) f(Pt)) + Gsolv(lacvp** d(S)) + ZPE(lacvp** d(S)) + ΔH(500)(lacvp** d(S)). For gas phase molecules an empirical correction of 0.4*Strans/rot was added to account for the higher translational and rotational entropy in the gas phase compared to the solution phase. Using the empirical correction we found excellent agreement for free energy of solvation of the few species (solvation water and sulfuric acid in sulfuric acid) where we have experimental data for the sulfuric acid medium. Our value of 0.4 is similar to the 0.46 reported by Wertz for solvation in water.[11] All species are calculated at 1 M or 1 atm except sulfuric acid, which is corrected to 18 M to reflect typical experimental conditions. For all complexes the first protonation of the bpym ligand is calculated to be favorable. For a few, namely the most electron rich platinum(II) complexes, the second protonation is also favorable.

5.2 Structure Coordinates

$[(H_2bpym)Pt^{II}ClCH_3]^{2+}$

$E_{lacv3p**++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1147.53992921979

G_{solv} = -0.3428968

Pt1	-0.2144374643	0.0796851473	-0.2527294363
N2	1.8167441063	-0.1313275804	-0.0533134413
N3	0.4802438879	2.1722295315	-0.1381113628
C4	-0.6404977752	-1.9262119732	-0.3588346720
C5	1.8022245258	2.2759506107	-0.0172910840
C6	2.5432073116	1.0006051144	0.0339457754
N7	3.8837944649	0.9419760389	0.1645486034
N8	2.3945187564	3.4866955643	0.0533540382
C9	-0.2719423291	3.2916329720	-0.1881002364
C10	1.6822365347	4.6292399045	0.0065623267
C11	2.4682188390	-1.3222454176	-0.0015704451
C12	4.5602608815	-0.2183720595	0.2179262699
C13	3.8435844544	-1.4036298461	0.1353397256
C14	0.3020821136	4.5547955008	-0.1170977286
H15	1.8580972186	-2.2138817437	-0.0729922231
H16	5.6374800934	-0.1551829589	0.3226285823
H17	-1.3436265359	3.1452446148	-0.2860855880
H18	2.2410980318	5.5563021145	0.0692017344
H19	-0.3024430244	5.4537548333	-0.1562978072
H20	4.3415556878	-2.3655982024	0.1739238382
H21	-1.7108936897	-2.0977218772	-0.4985537849
H22	-0.3212922466	-2.4119714328	0.5721497045
H23	-0.0980890180	-2.3637605996	-1.2067487605
Cl24	-2.4967352898	0.5779710188	-0.4704737891
H25	4.4376744707	1.7965560283	0.2273694252

H26	3.4063443089	3.5814954766	0.1447340856

$[(Hbpym)Pt^{IV}Cl_2(HSO4)_2]^{2+}$

$E_{lacv3p**++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -2967.25687239167

G_{solv} = -0.1701495

Pt1	-2.7085916645	-4.4169701258	1.1750555599
N2	-1.8503346895	-5.9300880272	2.2751821347
N3	-2.3758225294	-5.8270877446	-0.3582823475
C4	-1.7892246307	-6.9316361692	0.1021469576
C5	-1.5043783412	-7.0196623377	1.5437304651
N6	-0.9512603873	-8.1089512131	2.0262098314
N7	-1.4658001208	-7.9261773060	-0.7328114286
C8	-2.6464783412	-5.6873713347	-1.6705363136
C9	-1.7111335761	-7.8493763858	-2.0568210986
C10	-1.6252955736	-5.9510933904	3.5996402390
C11	-0.7142188664	-8.1487241093	3.3486611110
C12	-1.0442662184	-7.0780151002	4.1785894787
C13	-2.3174200425	-6.7053992357	-2.5607518148
H14	-1.9094763257	-5.0758748859	4.1725778708
H15	-0.2555170857	-9.0532593807	3.7388361623
H16	-3.1148654563	-4.7581511633	-1.9808790937
H17	-1.4130030688	-8.6990623856	-2.6620038524
H18	-2.5287656079	-6.6052320880	-3.6197844989
H19	-0.8589809169	-7.1058764530	5.2469992148
Cl20	-0.5829923247	-3.4924820385	0.7333779081
Cl22	-2.9359965695	-2.9772125007	3.0152846034
S25	-4.3429558216	-1.8882241675	-0.2300875589
O26	-3.6292596018	-0.7377816560	-0.6944553954
O27	-5.0372703175	-1.7648220127	1.0382887056
O28	-3.4457770802	-3.1423155733	-0.2671282306

O29	-5.3943466092	-2.2265608800	-1.3563677364
H30	-5.9076341063	-3.0242518955	-1.0806743641
S33	-5.9257727772	-4.9886140944	1.3319140637
O34	-6.7845121424	-6.0478135517	1.7763391665
O35	-6.0339696323	-4.5603611570	-0.0489673412
O36	-4.4821303849	-5.4272865774	1.6561651695
O37	-6.2237035485	-3.7656473558	2.2673133501
H38	-5.8367223733	-2.9281083932	1.8813537792
H34	-1.0163708139	-8.7586136013	-0.3328092210

$[(H_2bpym)Pt^{II}ClCH_3 \cdot\cdot (Hbpym)Pt^{IV}Cl_2(HSO4)]^{3+}$

$E_{lacv3p**++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -3414.34138130096

G_{solv} = -0.5116223

Imaginary freq = -417.15

Pt1	0.0000000000	0.0000000000	0.0000000000
Cl2	0.0000000000	0.0000000000	2.6837294734
Pt3	0.3897318041	0.0000000000	5.3280810920
N4	-0.5250021367	1.7557733489	5.8920431293
N5	2.0373379815	1.2923922699	5.2823549470
C6	1.7371322269	2.5073302955	5.7497493441
C7	0.3402581947	2.7793323763	6.1173693400
N8	0.0402285645	3.9380968859	6.6634248407
N9	2.6869262963	3.4391288718	5.9027980731
C10	3.3145297087	0.9935416579	4.9597626848
C11	3.9758219451	3.1975043375	5.5954740698
C12	-1.8090746269	1.9382899671	6.2551940357
C13	-1.2343248457	4.1229816139	7.0454703936
C14	-2.1999749339	3.1361548750	6.8505393399
C15	4.3195148452	1.9447616838	5.1015801473
H16	-2.4960605481	1.1165973824	6.0857921705

H17	-1.4758184136	5.0721262692	7.5163988905
H18	3.5037917049	-0.0144408017	4.6050068725
H19	4.6819091300	4.0041209242	5.7629601125
H20	5.3479424091	1.7104035761	4.8503587351
H21	-3.2291909111	3.2789039012	7.1619299599
Cl22	-1.5106888793	-1.3310670968	5.5932403018
N23	0.8373432952	-1.9987299749	-0.7046615942
N24	-1.7325384611	-1.0809174026	-0.4636569630
C25	-1.5400152962	-2.2843825349	-1.0622909724
C26	-0.1440544173	-2.7513782533	-1.1872001181
N27	0.0990328825	-3.9463570304	-1.7522289315
N28	-2.4901010865	-3.0759363953	-1.5234545663
C29	-3.0087354377	-0.6825765563	-0.2976738998
C30	-3.7607644854	-2.6731152817	-1.3743233022
C31	2.1031838206	-2.4566690971	-0.7648724819
C32	1.3464954664	-4.4459910653	-1.8371053781
C33	2.3975023640	-3.6969975423	-1.3271701119
C34	-4.0662532772	-1.4692579542	-0.7430310178
H35	2.8759459332	-1.8121890638	-0.3561645120
H36	1.4578181325	-5.4219692064	-2.2972734972
H37	-3.1776645456	0.2706349592	0.1888982054
H38	-4.5359105360	-3.3313042013	-1.7564986718
H39	-5.0906251088	-1.1443202855	-0.5966990429
H40	3.4143500893	-4.0703503540	-1.3646749860
H41	-0.7059166589	-4.4789371961	-2.1000370514
Cl42	2.0898960297	1.0163768303	0.2537752426
C43	-0.9695553030	1.7892623277	0.3565918275
H44	-1.7806586375	1.6371501734	1.0713562977
H45	-0.2541291202	2.5135882699	0.7446064366
H46	-1.3536719675	2.0971542396	-0.6224817563

S48	1.9333962974	-2.1201075936	6.6376119878
O49	1.3391843482	-1.1373461847	7.5320594510
O50	3.3389045759	-2.3946446632	6.7674535974
O51	1.6216385345	-1.6824434767	5.1887601796
O52	1.1065736078	-3.4380724601	6.8967963608
H53	1.4577429499	-4.1976723705	6.3890288134
H60	2.4003772153	4.3496069114	6.2826279565

$[(Hbpym)Pt^{IV}Cl_2(HSO4)CH_3]^+$

$E_{lacv3p**++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -2307.38944491057

G_{solv} = -0.1506518

Pt1	-0.2211579935	-0.0253461342	-0.3540488062
N2	1.8519268207	-0.1619538347	-0.1164094795
N3	0.4204713626	2.2027977803	-0.0905798683
C4	-0.5426399644	-2.0768610252	-0.5363563252
C5	1.7311011679	2.2535292498	0.0877890155
C6	2.5219356407	1.0017201619	0.0633275899
N7	3.8285000994	1.1061510901	0.2172298137
N8	2.3659420982	3.4218519845	0.2899677675
C9	-0.2929316329	3.3430657252	-0.0721981154
C10	1.6972375289	4.5901987572	0.3251477070
C11	2.5672364888	-1.3003772281	-0.1318023788
C12	4.5522486742	-0.0228938015	0.1924508122
C13	3.9494851185	-1.2671633551	0.0228073259
C14	0.3214444637	4.5756123021	0.1405978892
H15	2.0345154937	-2.2338421612	-0.2688081724
H16	5.6278914290	0.0795779569	0.3083352735
H17	-1.3640215959	3.2537305360	-0.2306915521
H18	2.2815419977	5.4878970902	0.4957950931
H19	-0.2520814582	5.4952313076	0.1603321738

H20	4.5242290539	-2.1866105547	0.0057989320
H26	-1.6077450943	-2.2249204178	-0.7006377305
H27	-0.2231365029	-2.5076141001	0.4115877292
H28	0.0452317710	-2.4180101129	-1.3877556625
Cl36	-2.5320003324	0.3934767788	-0.6276659876
Cl26	0.0546986332	0.1138499400	-2.6904951720
S33	-1.4360615460	-0.5275239316	2.6263989109
O34	-0.9832281562	-0.4491248804	3.9894983203
O35	-2.0159691910	-1.7617717053	2.1636547985
O36	-0.2714023558	-0.0726772679	1.7334960719
O37	-2.5281599554	0.6250457037	2.5052854762
H38	-2.9329901079	0.6151003695	1.6090532509
H32	3.3832328236	3.3957921856	0.4172888048

$[(Hbpym)Pt^{II}Cl(HSO_4)]^+$

$E_{lacv3p**++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -1807.23878632258

G_{solv} = -0.1684679

Pt1	-0.1974369198	0.2757412902	-0.2018467890
N2	1.8149185420	-0.0793723654	-0.0878986165
N3	0.4720619054	2.1930001671	-0.2083019236
C4	1.8237941322	2.3178918411	-0.1430888947
C5	2.5454986094	1.0420355722	-0.0819183316
N6	3.8825086323	0.9934432813	-0.0162389598
N7	2.4980497822	3.4495897670	-0.1268493935
C8	-0.2482907674	3.3317881494	-0.2608886718
C9	1.7858397917	4.5857814134	-0.1797703831
C10	2.4359201368	-1.2773304257	-0.0299980666
C11	4.5504154849	-0.1753375411	0.0470223301
C12	3.8221237328	-1.3568620050	0.0394205014
C13	0.3930061809	4.5666732510	-0.2482295606

H14	1.7995140044	-2.1555537472	-0.0391498804
H15	5.6321868176	-0.1243776487	0.1005021898
H16	-1.3263202240	3.2354298684	-0.3120555149
H17	2.3426173884	5.5184736336	-0.1658487137
H18	-0.1862852376	5.4824533424	-0.2899894666
H19	4.3190285152	-2.3191103760	0.0882172824
Cl20	-2.4912849371	0.8436486761	-0.3335714729
H21	4.3894422856	1.8850042908	-0.0142130799
S22	-1.7153950780	-2.5232219134	0.3829250299
O23	-1.9413901940	-2.0676569257	1.7329840333
O24	-1.4952039666	-3.9279770933	0.1660802259
O25	-0.5769226230	-1.7536417548	-0.2830484880
O26	-3.0012653484	-2.1875317190	-0.4946596888
H27	-3.1790230149	-1.2211466413	-0.4710131390

$[(H_2bpym)Pt^{II}Cl_2CH_3$ - - $(Hbpym)Pt^{IV}Cl_2(HSO4)_2]^{2+}$

$E_{lacv3p**++(+\ 2df\ on\ S,\ f\ on\ Pt)}$ = -4575.32885473300

G_{solv} = -0.3819829

Pt29	0.0000000000	0.0000000000	0.0000000000
Cl28	0.0000000000	0.0000000000	2.6064499616
Pt1	0.9113338222	0.0000000000	4.9389894400
N2	-0.5188634501	-1.1993844939	5.7925937212
N3	-0.3693018605	1.4665992031	5.7116546984
C4	-1.3784041953	0.9400307282	6.4059220238
C5	-1.4944844657	-0.5248529259	6.4517278295
N6	-2.4947340722	-1.0702880435	7.1107764095
N7	-2.2514595858	1.7251815004	7.0512041184
C8	-0.2082763803	2.8040241007	5.6631233395
C9	-2.1433333033	3.0689692647	7.0358080314
C10	-0.5671287392	-2.5432612564	5.8154202730

C11	-2.5565609791	-2.4114500180	7.1324082544
C12	-1.5962222883	-3.1932071569	6.4917507054
C13	-1.0981483459	3.6452065341	6.3265010847
H14	0.2291118210	-3.0681783609	5.3032824402
H15	-3.3872672765	-2.8563462303	7.6732696692
H16	0.6392334214	3.1723081467	5.0931050110
H17	-2.8870167279	3.6299807434	7.5917549783
H18	-0.9740003162	4.7223229487	6.2961962546
H19	-1.6377541595	-4.2766234694	6.5134564543
Cl22	2.2583904353	-1.8110325613	4.2379898246
Cl59	0.7745048946	-0.9729226218	-2.9387544500
N30	2.1183005687	-0.8154301119	-0.0121659513
N31	-0.2693099438	-2.0726424583	-0.2364367598
C32	0.8365187503	-2.7510875082	-0.5940749940
C33	2.1505396130	-2.0854933206	-0.3938060261
N34	3.3250977303	-2.7310939782	-0.5324842072
N35	0.7356382883	-4.0198782550	-1.0298747456
C36	-1.4687831422	-2.6788262629	-0.3191866280
C37	-0.4543330395	-4.6418124616	-1.1855983762
C38	3.2642550939	-0.1441553730	0.1890534578
C39	4.5036108536	-2.0912682876	-0.3772116374
C40	4.5013382396	-0.7585416061	-0.0093721597
C41	-1.6039772334	-3.9745546312	-0.8103609298
H42	3.1752734891	0.8883567726	0.5094301660
H43	5.3985637518	-2.6800931164	-0.5436151784
H44	-2.3325533034	-2.1027833615	-0.0041270507
H45	-0.4283602110	-5.6499532884	-1.5845732751
H46	-2.5787370603	-4.4409610055	-0.8973049739
H47	5.4331296217	-0.2215872575	0.1257936609
H49	3.3733649842	-3.7236573954	-0.7532268310

Cl50	0.5509048110	2.2678860956	0.0284785098
C51	-1.9935501709	0.5081203062	-0.1126763941
H52	-2.5225060675	0.0512527135	0.7281418308
H53	-2.0989443727	1.5927573925	-0.0721309821
H54	-2.3630669211	0.1266935307	-1.0701112911
S25	3.5921309331	1.6407026761	3.8832452185
O26	3.7824616270	1.9805214122	2.5007533728
O27	4.3505250557	0.5037668117	4.3803699344
O28	2.1048441336	1.5261665993	4.2243504816
O29	4.0092807636	2.9139005127	4.7145918652
H30	3.8792434353	2.6917414879	5.6847184674
O36	1.8512408624	0.1698979762	7.1895915599
S33	3.1951019630	0.6421458249	7.6182015943
O34	3.4122547921	0.4619742766	9.0354441020
O35	3.4708404814	1.9983473147	7.1287905847
O37	4.2613628378	-0.3159676270	6.9201905521
H38	4.3162612178	-0.1068997939	5.9501748440
H60	-3.0082703812	1.2673264746	7.5719839465
H61	1.5653434645	-4.5518633239	-1.2901859344

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