Electronic Supplemental Information

Platinum Complexes of Cationic Ligands for the Aerobic Oxidation of "Inert" Perfluoro Substituted Alcohols

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Experimental Details

$Pt(DMSO)_2Cl_2$ was prepared according to a known procedure.[S1]

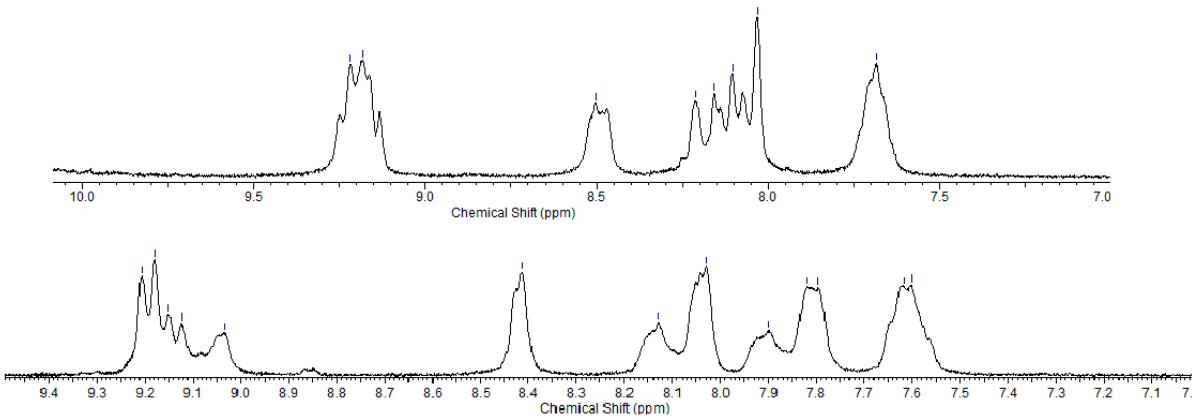
1,10-phenanthroline-5,6-dione was prepared according to a known procedure.[S2] ^{1}H-NMR in $CDCl_3$ (δ *9.13 [dd, 2H]; δ 8.52 [dd, 2H]; δ 7.60 [dd, 2H]*)

Dipyrido[3,2-a:2',3'-e]phenazine (dppz) was prepared according to a known procedure.[S3] ^{1}H-NMR (MeOD) *δ 9.16 [dd, 2H]; δ 8.96 [dd, 2H] ; δ 8.04 [dd, 2H]; δ 7.85 [dd, 2H]; δ 7.67 [dd, 2H]*; ESI-MS *MW=282.2*, *m/z+1=283.03* is attributed to *$M+H^+$, $M+Na^+$=305.04, $2M+Na^+$=587.07.*

11-(tert-butyl)dipyrido[3,2-a:2',3'-c]phenazine (dppz-tBu) was prepared in a similar way. ^{1}H-NMR ($CDCl_3$) *δ 9.67 [dd, 1H]; δ 9.64 [dd, 1H] ; δ 9.28 [dd, 1H]; δ 9.27 [dd, 1H]; δ 7.79 [dd, 1H]; δ 7.82 [dd, 1H]; δ 8.28 [d, 1H] ; δ 8.29 [d, 1H]; δ 8.04 [dd, 1H]; δ 1.54 [s, 9H]*; ESI-MS *MW=338.4*, *m/z+1=339.09* is attributed to *$M+H^+$, $M+Na^+$=360.97, $2M+Na^+$=699.21.*

$Pt^{II}(dppz)Cl_2$. dppz (71 mg, 0.25 mmol) was dissolved in a minimal amount of EtOH at 80 °C and then mixed with $Pt(DMSO)_2Cl_2$ (116 mmg, 0.275 mmol) also dissolved in EtOH and the mixture was kept at boiling for 20-30 min. After cooling to room temperature, the solid product was separated and washed with cold ethanol until the liquid phase was clear. The solid was dried under high vacuum overnight to yield 125 mg $Pt^{II}(dppz)Cl_2$ (91% yield). **$Pt^{II}(dppz\text{-}tBu)Cl_2$** was similarly prepared in a 85% yield. Anal. Calcd for $C_{18}H_{10}Cl_2N_4PtH_2O$ (**$Pt^{II}(dppz)Cl_2 \bullet H_2O$**): C, 38.18; H, 2.14; N, 9.89. Found: C, 37.96; H, 2.01; N, 9.37. Anal. Calcd for $C_{22}H_{18}Cl_2N_4PtH_2O$ (**$Pt^{II}(dppz\text{-}tBu)Cl_2 \bullet H_2O$**): C, 42.45; H, 3.24; N, 9.00. Found: C, 42.42; H, 2.94; N, 8.91.

Catalytic Reactions. Reactions were carried out in 25 mL stainless steel autoclave equipped with a glass liner and a stirring magnet. In a typical experiment, the autoclave was charged with 2 mL TFE, 250 μL 98% H_2SO_4, 0.0033 mol% catalyst, and then the gases were added to the desired pressures. The autoclave was then heated to 150 °C and the reaction was run for 24 h. After cooling, the reaction mixture was analyzed by GC-MS for product identification and GC-TCD for quantification. Safety measures should be taken when running a under 15 bar O_2. Reactions were run in a room designed for this purpose and the autoclave was equipped with a 60 bar rupture disc to prevent explosion.



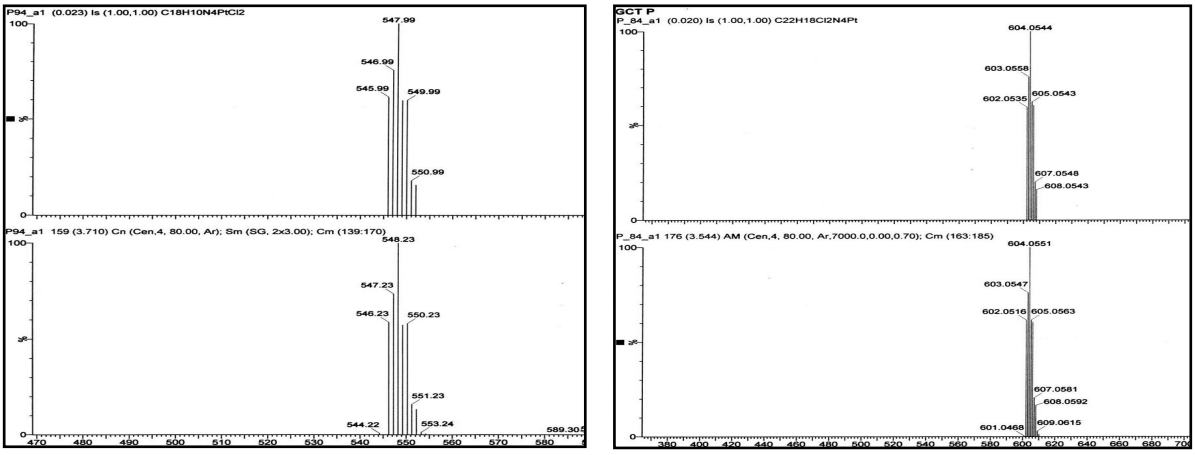


Figure S1. ^{1}H NMR spectra in D_2SO_4 of (**Pt^{II}(dppz)Cl_2**) (bottom) and (**Pt^{II}(dppz-tBu)Cl_2**) (top).

Figure S2. Field Desorption Mass Spectra of (**Pt^{II}(dppz)Cl_2**) (left) and (**Pt^{II}(dppz-tBu)Cl_2**) (right) showing experimental and calculated spectra.

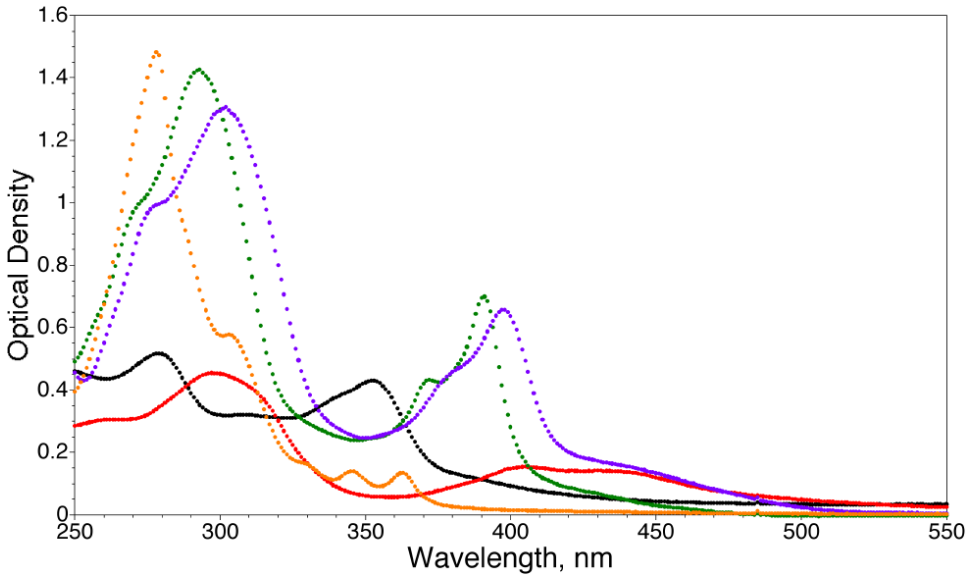


Figure S3. UV-vis spectra in concentrated H_2SO_4 of Pt^{II}(dppz)Cl_2 {black, 19.1 μM, (λ_{max} = 279, 309, 353; log ε = 4.43, 4.23, 4.35)}, Pt^{II}(dppz-tBu)Cl_2 {red, 9.6 μM (λ_{max} = 265, 297, 405, 432 ; log ε = 4.50, 4.67, 4.21, 4.16)}, dppz {green, 32.3 μM (λ_{max} = 293, 372, 391 ; log ε = 4.63, 4.11, 4.32)}, dppz-tBu {purple, 31.4 μM (λ_{max} = 302, 398 ; log ε = 4.62, 4.31)}, and Pt^{II}(phen)Cl_2 {orange, 52.4 μM (λ_{max} = 278, 303, 345, 363 ; log ε = 4.45, 4.04, 3.43, 3.41)}.

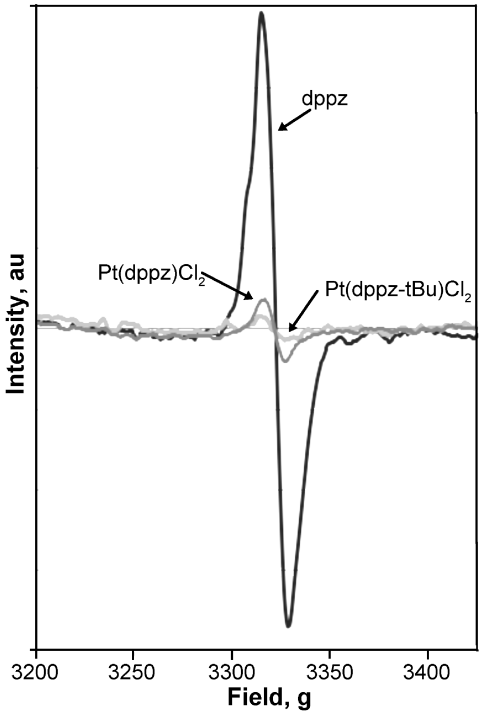


Figure S4. Room temperature X-band EPR spectra of dppz, $Pt^{II}(dppz)Cl_2$ and $Pt^{II}(dppz\text{-}tBu)Cl_2$ in concentrated H_2SO_4. The peak intensity, quantified with pitch, observed for dppz is consistent with the formation of a dppz radical cation as described in reference 13 (F. Hilgers, W. Kaim, A. Schulz and S. Zális, *J. Chem. Soc. Perkin Trans. 2*, 1994, 135-138.)

Computational Details

All calculations were carried out using GAUSSIAN09 C.01.[S4] Three DFT exchange-correlation functionals were used. The first is the M06 functional,[S5] a meta-hybrid GGA functional containing 27% Hartree-Fock exchange, which has been shown to have superior performance in the study of transition metal reactions.[S5-6] The second is the local version of the M06 family (M06-L).[S7] This functional was shown to provide similar performance as M06 for transitional metals.[S5-6] The third is the latest double-hybrid functional by Kozuch and Martin: DSD-PBEP86.[S8] This is a double-hybrid functional incorporating Perdew-Burke-Ernzerhof (PBE)[S9] DFT exchange with "exact" Hartree-Fock exchange, the Perdew-86 correlation with "exact" spin-component scaled[S10] second-order Møller-Plesset[S11] (SCS-MP2) correlation and an empirical dispersion correction[S12] – specifically Grimme's third version of his empirical dispersion correction (DFTD3)[S12d,13] with Becke-Johnson (BJ) dampening.[S13-14]

With these functionals, three basis sets were used. SDD(d) is the combination of the Huzinaga-Dunning double-ζ basis set[S15] on lighter elements, with extra polarization functions (*i.e.*, D95(d)) on second-row elements, with the Stuttgart-Dresden basis set-RECP combination[S16] on transition metals; diffuse functions were added to fluorine atoms (*i.e.*, D95V++).[S15] SDB-cc-pVDZ, combines the Dunning cc-pVDZ basis set[S17] on the main group elements and the Stuttgart-Dresden basis set-RECP[S16] on the transition metals with an added *f*-type polarization exponent taken as the average of the two *f*-exponents given in the appendix of ref S18. The third is cc-pV(D+d)Z-PP, which includes Dunning's cc-pVDZ[S17] on the main group elements, Wilson's c-pV(D+d)Z[S19] modification on second-row elements, and Peterson's cc-pVDZ-PP basis set-RECP[S20] on platinum.

Density fitting basis sets (DFBS),[S21] as implemented in GAUSSIAN09, were employed in order to improve the computational efficiency of the calculation. Because the use of DFBSs pre-

cludes the use of a hybrid DFT exchange-correlation functional, the local version of the M06 family (M06-L) was employed.[S7] This functional was shown to provide similar performance as M06 for transitional metals.[S5-6] The automatic DFBS generation algorithm built-in to GAUSSIAN09 was employed.

Electronic excitations were calculated using time-dependent DFT (TDDFT).[S22] Only the first five singlet excitations were considered. Świderek *et al*. showed that hybrid functions, including M06, predicted MLCT (metal-ligand charge transfer) excitations with reasonable accuracy for a series of iridium complexes.[S23]

Bulk solvent effects were approximated by single point energy calculations using a polarizable continuum model (PCM),[S24] specifically the integral equation formalism model (IEF-PCM)[S24a,b,25] with 2,2,2-trifluoroethanol (TFE) as the solvent as in the experiments. Truhlar and co-workers' empirically-parameterized Solvation Model-Dispersion (SMD)[S26] was also used.

Geometries were optimized using the default pruned (75,302) grid, while the "ultrafine" (i.e., a pruned (99,590)) grid was used for energy and solvation calculations.

Six types of charges were considered: (*i*) natural population analysis (NPA) charges[S27] were derived from natural bond order (NBO) analyses,[S27] (*ii*) Löwdin charges,[S28] (*iii*) Mulliken charges,[S29] (*iv*) atomic polar tensor (APT) charges,[S30] (*v*) Hirshfeld (stockholder) charges,[S31] and (*vi*) Truhlar's Charge Model 5 (CM5) charges based on the Hirshfeld population analysis.[S32] Three different bond order analyses were considered: (*i*) Wiberg,[S27,33] (*ii*) Mayer,[S34] and (*iii*) natural localized molecular orbital (NLMO)[S27,35] bond orders. These properties were calculated using GAUSSIAN09, with NBO 5.0[S36] where needed. CM5 charges were calculated using CM5PAC.[S37] While GAUSSIAN09 provides Hirshfeld charges, the charges on the hydrogen atoms are summed into the charges on the heavy atoms, and for this reason the Hirshfeld charges were taken from the results of CM5PAC.

Table S1. **Dppz**-ligand protonation energies (ΔG_{423}, kcal/mol, SMD(TFE)-DSD-PBEP86/cc-pV(D+d)Z-PP//DF-M06-L/SDD(d) level of theory) of the bisulphate and sulphuric acid complexes (*i.e.*, the reaction energy for the reactions (*i*) $[(dppz)Pt(TFE)(H_2O)]^{2+} + H_3O^+ \rightarrow [(H^+N\text{-}dppz)Pt(TFE)(H_2O)]^{3+} + H_2O$ and (*ii*) $[(H\text{-}^+N\text{-}dppz)Pt(TFE)(H_2O)]^{3+} + H_3O^+ \rightarrow [(H_2\text{-}N,N'\text{-}dppz)Pt(TFE)(H_2O)]^{4+} + H_2O$), and the analogous reactions with the *bis*-TFE complexes.

	H-$^+$*N*-dppz (anti)	**H-$^+$*N*-dppz (syn)**	**H-$^+$*N*-dppz (TFE)$_2$**
(*i*)	-4.9	-5.2	-1.9
(*ii*)	13.4	13.7	11.3

[a] throughout syn and anti refer to the Pt-TFE bond on the same side or opposite side of the molecule relative to the N-H bond in H-*N*-dppz

Table S2. Coordinated sulphuric acid deprotonation energies (ΔG_{423}, kcal/mol, SMD(TFE)-DSD-PBEP86/cc-pV(D+d)Z-PP//DF-M06-L/SDD(d) level of theory; *i.e.*, the energy for the reaction $[LPt(TFE)(H_2SO_4)]^{m+} + H_2O \rightarrow [LPt(TFE)(HSO_4)]^{(m-1)+} + H_3O^+$).

	L = phen	**L = H-$^+$*N*-dppz (anti)**	**L = H-$^+$*N*-dppz (syn)**	**L = dppz**
ΔG_{423}	-6.5	-12.4	-10.9	-11.4

Table S3. Ligand exchange energies (ΔG_{423}, kcal/mol, SMD(TFE)-DSD-PBEP86/cc-pV(D+d)Z-PP//DF-M06-L/SDD(d) level of theory) of the bisulphate and sulphuric acid complexes with TFE (*i.e.*, the reaction energy for the reaction $[LPt(TFE)(H_xSO_4)]^{m+}$ + TFE → $[LPt(TFE)_2]^{(m+1)+}$ + H_xSO_4 where x=1 or 2).

	L = phen	**L = H-$^+$*N*-dppz (anti)**
H_2SO_4	-1.3	-2.6
w.r.t. HSO_4^- complex	—	-7.9
HSO_4^-	21.0	25.3
w.r.t. HSO_4^- complex	—	20.0

Table S4. First five single TDDFT excitations (H = HOMO, L = LUMO) in $[(\mathbf{L})Pt(HSO_4)(TFE)]^{n+}$ complexes at the PCM(TFE)-M06/cc-pV(D+d)Z-PP//DF-M06-L/SDD(d) level of theory.

L = phen		**L = dppz**	
H-1 → L+2 (0.65)	2.98 eV, 416 nm	H-2 → L+3 (-0.68)	2.95 eV, 420 nm
H-2 → L+2 (0.44) H → L +2 (0.48)	3.20 eV, 388 nm	H-3 → L+3 (0.57)	3.18 eV, 389 nm
H-1 → L (0.64)	3.36 eV, 369 nm	H → L (0.66)	3.21 eV, 386 nm (*f* = 0.0273)
H → L (0.53)	3.48 eV, 357 nm (*f* = 0.0226)	H-4 → L (0.62)	3.24 eV, 382 nm
H-4 → L+2 (-0.41) H-2 → L+2 (0.42)	3.29 eV, 355 nm	H-2 → L (0.48) H-2 → L+1 (-0.46)	3.28 eV, 378 nm
L = H-$^+$*N*-dppz (anti)		**L = H-$^+$*N*-dppz (syn)**	
H → L (0.70)	2.60 eV, 477 nm	H → L (0.70)	2.60 eV, 478 nm
H-2 → L (0.53)	2.73 eV, 453 nm (*f* = 0.0288)	H-3 → L (-0.41) H-1 → L (0.55)	2.73 eV, 454 nm (*f* = 0.0297)
H-1 → L (0.55)	2.90 eV, 427 nm (*f* = 0.0737)	H → L+3 (-0.55)	2.93 eV, 423 nm
H → L+3 (-0.67)	2.94 eV, 422 nm, (*f* = 0.0171)	H-2 → L (0.40) H → L+3 (0.43)	2.96 eV, 419 nm
H-3 → L (0.63)	3.05 eV, 406 nm (*f* = 0.1214)	H-3 → L ().48) H-2 → L (-0.42)	3.00 eV, 414 nm, (*f* = 0.2271)

Table S5. FMO energies for [(**L**)Pt(HSO_4)(TFE)]$^{n+}$ (eV, PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory).

	L = phen	**L = H-*N*-dppz (anti)**	**L = H-*N*-dppz (syn)**	**L = dppz**
HOMO	-7.63	-7.92	-7.92	-7.38
LUMO	-3.07	-4.56	-4.56	-3.29
Gap	4.56	3.36	3.35	4.08

Table S6. Frontier Molecular Orbitals for [(**L**)Pt(HSO_4)(TFE)]$^{n+}$ (PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory).

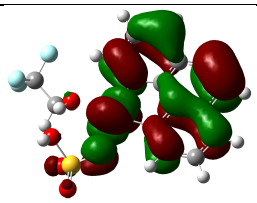
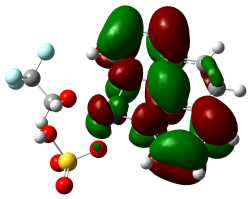
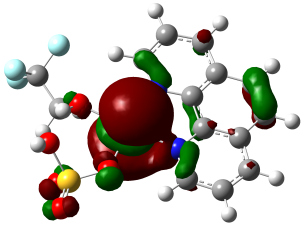
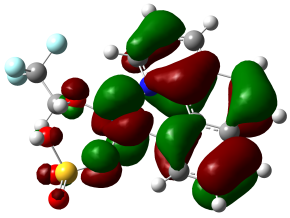
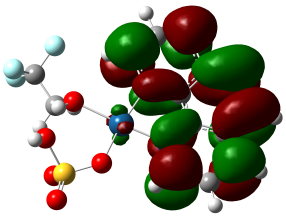
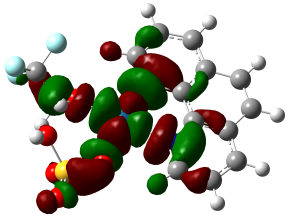
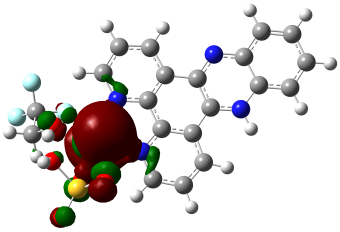
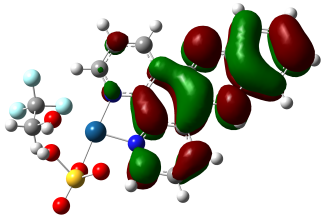
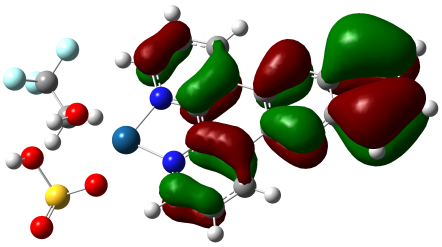
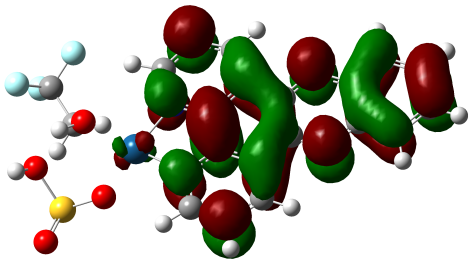
	HOMO	**LUMO**
L = phen		
	HOMO-1 	HOMO-2 
	LUMO+1 	LUMO+2 
L = H-*N*-dppz (anti)		
L = dppz		

Table S7. Charges on Pt for [(**L**)Pt(TFE)(HSO_4)]$^{m+}$

Class of Charge	L = phen	L = H-$^+$***N***-dppz (anti)	L = H-$^+$***N***-dppz (syn)	L = dppz
Mulliken[a]	0.548	0.489	0.488	0.560
APT[b]	0.782	0.891	0.889	0.781
NPA[a]	0.714	0.704	0.704	0.721
Löwdin[a]	-0.633	-0.730	-0.730	-0.626
Hirshfeld[a]	0.139	0.138	0.138	0.145
CM5[a]	0.490	0.495	0.495	0.495

[a] At the PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory. [b] At the DF-M06-L/SDD(d) level of theory.

Table S8. Bond orders and bonds lengths (Å) of the Pt-X bond in [(**L**)Pt(TFE)(HSO_4)]$^{m+}$ (PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory).

		L = phen	L = H-$^+$***N***-dppz (anti)	L = H-$^+$***N***-dppz (syn)	L = dppz
Wiberg	HSO_4	0.4426	0.4521	0.4569	0.4416
	TFE	0.3439	0.3596	0.3567	0.3440
Mayer	HSO_4	0.553	0.587	0.590	0.553
	TFE	0.445	0.475	0.474	0.447
Bond Length	HSO_4	2.079	2.066	2.060	2.083
	TFE	2.131	2.128	2.132	2.134

Table S9. Charges on Pt for [(L)Pt(TFE)(H_2SO_4)]$^{m+}$

Class of Charge	L = phen	L = H-$^+$***N***-dppz (anti)	L = H-$^+$***N***-dppz (syn)	L = dppz
Mulliken[a]	0.592	0.639	0.638	0.662
APT[b]	0.854	0.967	0.970	0.820
NPA[a]	0.759	0.782	0.782	0.784
Löwdin[a]	-0.586	-0.567	-0.567	-0.504
Hirshfeld[a]	0.205	0.220	0.219	0.217
CM5[a]	0.543	0.559	0.559	0.555

[a] At the PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory. [b] At the DF-M06-L/SDD(d) level of theory.

Table S10. FMO energies for [(L)Pt(TFE)(H_2SO_4)]$^{m+}$ (eV, PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory).

	L = phen	L = H-$^+$***N***-dppz (anti)	L = H-$^+$***N***-dppz (syn)	L = dppz
HOMO	-7.91	-8.31	-8.31	-6.73
LUMO	-3.30	-4.68	-4.67	-3.48
Gap	4.61	3.63	3.63	3.25

Table S11. Bond orders and bonds lengths (Å) of the Pt-X bond $[(\mathbf{L})Pt(TFE)(H_2SO_4)]^{m+}$ (PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory).

		L = phen	**L = H-$^{+}$*N*-dppz (anti)**	**L = H-$^{+}$*N*-dppz (syn)**	**L = dppz**
Wiberg	$H_2SO_4^-$	0.3132	0.3286	0.3338	0.3154
	TFE	0.3154	0.3292	0.3252	0.3141
Mayer	$H_2SO_4^-$	0.405	0.419	0.422	0.404
	TFE	0.407	0.416	0.415	0.399
Bond Length	$H_2SO_4^-$	2.186	2.172	2.163	2.180
	TFE	2.153	2.142	2.148	2.137

Table S12. First five single TDDFT excitations (H = HOMO, L = LUMO) in $[(L)Pt(H_2SO_4)(TFE)]^{n+}$ complexes at the PCM(TFE)-M06/cc-pV(D+d)Z-PP//DF-M06-L/SDD(d) level of theory.

L = phen		**L = dppz**	
H-1 → L+1 (0.70)	2.50 eV, 496 nm	H-2 → L+2 (0.71)	2.49 eV, 498 nm
H-3 → L+1 (0.42) H-2 → L+1 (0.52)	2.95 eV, 421 nm	H-4 → L+2 (0.58)	2.93 eV, 423 nm
H-4 → L+1 (0.50) H → L+1 (-0.44)	3.07 eV, 403 nm	H-5 → L+2 (-0.51)	3.07 eV, 404 nm
H-5 → L+1 (0.69)	3.45 eV, 359 nm	H → L (0.63)	3.16 eV, 392 nm (*f* = 0.0324)
H-1 → L (0.68)	3.49 eV, 355 nm	H-2 → L (0.51) H-2 → L+1 (0.48)	3.23 eV, 384 nm
L = H-$^{+}$*N*-dppz (anti)		**L = H-$^{+}$*N*-dppz (syn)**	
H → L+3 (0.70)	2.45 eV, 506 nm	H → L+3 (0.70)	2.46 eV, 505 nm
H-1 → L (0.67)	2.73 eV, 454 nm (*f* = 0.0264)	H-1 → L (0.67)	2.73 eV, 454 nm (*f* = 0.0265)
H → L (0.68)	2.85 eV, 435 nm	H → L (0.69)	2.85 eV, 434 nm
H-2 → L+3 (0.52)	2.94 eV, 422 nm	H-3 → L+3 (0.63)	2.96 eV, 419 nm
H-2 → L (0.67)	3.07 eV, 404 nm (*f* = 0.2230)	H-4 → L+3 (0.45) H-2 → L+3 (0.44)	3.12 eV, 398 nm (*f* = 0.0228)

Table S13. Charges on Pt for $[(\mathbf{L})Pt(TFE)_2]^{m+}$

Class of Charge	**L = phen**	**L = dppz**	**L = H-*N*-dppz**	**L = H-*N*-$^{+}$dppz (HSO_4^-)**	**L=H_2-$^{++}$*N,N'*-dppz**
Mulliken[a]	0.541	0.560	0.588	0.522	0.529
APT[b]	0.857	0.924	0.969	0.940	0.543
NPA[a]	0.733	0.741	0.756	0.746	0.738
Löwdin[a]	-0.652	-0.642	-0.635	-0.674	-0.640
Hirshfeld[a]	0.189	0.197	0.204	0.199	0.198
CM5[a]	0.526	0.533	0.544	0.540	0.527

[a] At the PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory. [b] At the DF-M06-L/SDD(d) level of theory.

Table S14. FMO energies for [(**L**)Pt(TFE)$_2$]$^{m+}$ (eV, PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory).

	L = phen	**L = dppz**	**L = H-*N*-dppz**	**L = H-$^+$*N*-dppz (HSO_4^-)**	**L = H_2-$^{++}$*N,N'*-dppz**
HOMO	-7.96	-7.47	-8.37	-7.85	-5.40
LUMO	-3.34	-3.48	-4.69	-4.24	-3.28

[a] 1st two occupied MOs have primarily HSO_4^- character; high complex based MO is HOMO-2 at -8.23 eV.

Table S15. Bond orders and bonds lengths (Å) of the Pt-X bond for [(**L**)Pt(TFE)$_2$]$^{m+}$ (PCM(TFE)-M06/SDB-cc-pVDZ//DF-M06-L/SDD(d) level of theory).[a]

		L = phen	**L = dppz**	**L = H-$^+$*N*-dppz**	**L = H-$^+$*N*-dppz (HSO_4^-)**	**L = H_2-$^{++}$*N,N'*-dppz**
Wiberg	*anti*	0.30	0.30	0.31	0.30	0.29
	syn	0.31	0.31	0.32	0.32	0.31
Mayer	*anti*	0.40	0.40	0.41	0.40	0.40
	syn	0.42	0.41	0.42	0.42	0.41
Bond	*anti*	2.185	2.186	2.177	2.182	2.208
Length	*syn*	2.159	2.168	2.146	2.154	2.173

[a] In the asymmetric H-$^+$*N*-dppz complexes, *syn* and *anti* refer to the Pt-X bond on the same side or opposite side of the molecule as the dppz N-H bond; in the other cases, the two numbers just refer to each of the TFE ligands.

Additional References

S1. J. H. Price, A. N. Williamson, R. F. Schramm, B. B. Wayland, *Inorg. Chem.* **1972**, *11,* 1280-1284.

S2. M. Yamada, Y. Tanaka, Y. Yoshimoto, S. Kuroda, I. Shimao, *Bull. Chem. Soc. Japan* **1992**, *65,* 1006-1011.

S3. J. E. Dickerson, L. A. Summers, *Aust. J. Chem.* **1970,** *23,* 1023-1027.

S4. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2011.2.

S5. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008,** *120*, 215-241.

S6. Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008,** *41*, 157-167.

S7. Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* **2006,** *125*, 194101.

S8. S. Kozuch, J. M. L. Martin, *Phys. Chem. Chem. Phys.* **2011,** *13*, 20104-20107.

S9. (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996,** *77*, 3865-3868; (b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997,** *78*, 1396; (c) C. Adamo, V. Barone, *J. Chem. Phys.* **1999,** *110*, 6158-6170.

S10. (a) S. Grimme, *J. Chem. Phys.* **2003,** *118*, 9095-9102; (b) Å. Szabados, *J. Chem. Phys.* **2006,** *125*, 214105.

S11. C. Møller, M. S. Plesset, *Phys. Rev.* **1934,** *46*, 618-622.

S12. (a) S. Grimme, *J. Comput. Chem.* **2006,** *27*, 1787-1799; (b) T. Schwabe, S. Grimme, *Phys. Chem. Chem. Phys.* **2007,** *9*, 3397-3406; (c) T. Schwabe, S. Grimme, *Acc. Chem. Res.* **2008,** *41*, 569-579; (d) S. Grimme, J. Antony, S. Ehrlich, H. Kreig, *J. Chem. Phys.* **2010,** *132*, 154104.

S13. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011,** *32*, 1456-1465.

S14. (a) E. R. Johnson, A. D. Becke, *J. Chem. Phys.* **2005,** *123*, 024101; (b) A. D. Becke, E. R. Johnson, *J. Chem. Phys.* **2005,** *122*, 154104; (c) E. R. Johnson, A. D. Becke, *J. Chem. Phys.* **2006,** *124*, 174104.

S15. T. H. Dunning Jr., P. J. Hay, In *Modern Theoretical Chemistry 3. Methods of Electronic Structure Theory*, H. F. Schaefer III, Ed. Plenum Press: New York NY, 1976; Vol. 3, pp 1-28.

S16. M. Dolg, In *Modern Methods and Algorithms of Quantum Chemistry*, J. Grotendorst, Ed. John von Neumann Institute for Computing: Jülich, 2000; Vol. 3, pp 507-540.

S17. T. H. Dunning Jr., *J. Chem. Phys.* **1989,** *90*, 1007-1023.

S18. J. M. L. Martin, A. Sundermann, *J. Chem. Phys.* **2001,** *114*, 3408-3420.

S19. A. K. Wilson, D. E. Woon, K. A. Peterson, T. H. Dunning Jr., *J. Chem. Phys.* **1999,** *110*, 7667-7676.

S20. D. Figgen, K. A. Peterson, M. Dolg, H. Stoll, *J. Chem. Phys.* **2009,** *130*, 164108.

S21. (a) B. I. Dunlap, *J. Chem. Phys.* **1983,** *78*, 3140-3142; (b) B. I. Dunlap, *J. Mol. Struct. (THEOCHEM)* **2000,** *529*, 37-40.

S22. (a) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996,** *256*, 454-464; (b) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998,** *108*, 4439-4449; (c) R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998,** *109*, 8128-8224; (d) C. Van

Caillie, R. D. Amos, *Chem. Phys. Lett.* **1999,** *308*, 249-255; (e) C. Van Caillie, R. D. Amos, *Chem. Phys. Lett.* **2000,** *317*, 159-164; (f) F. Filipp, R. Ahlrichs, *J. Chem. Phys.* **2002,** *117*, 7433-7447; (g) G. Scalmani, M. J. Frisch, B. Mennucci, J. Tomasi, R. Cammi, V. Barone, *J. Chem. Phys.* **2006,** *124*, 094107.

S23. K. Świderek, P. Paneth, *J. Phys. Org. Chem.* **2009,** *22*, 845-856.

S24. (a) B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997,** *106*, 5151-5158; (b) E. Cancès, E.; B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997,** *107*, 3032-3041; (c) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* **1998,** *286*, 253-260; (d) M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* **2002,** *117*, 43-54.

S25. (a) B. Mennucci, E. Cancès, J. Tomasi, *J. Phys. Chem. B* **1997,** *101*, 10506-10517; (b) B. Mennucci, J. Tomasi, E. Cancès, *J. Mol. Struct. (THEOCHEM)* **1999,** *464*, 211-226.

S26. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009,** *113*, 6378-6396.

S27. A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988,** *88*, 899-926.

S28. (a) P.-O. Löwdin, *J. Chem. Phys.* **1950,** *18*, 365-375; (b) L. C. Cusachs, P. Politzer, *Chem. Phys. Lett.* **1968,** *1*, 529-531; (c) P.-O. Löwdin, *Adv. Quantum Chem.* **1970,** *5*, 185-199.

S29. R. S. Mulliken, *J. Chem. Phys.* **1955,** *23*, 1833-1840.

S30. J. Cioslowski, *J. Am. Chem. Soc.* **1989,** *111*, 8333-8336.

S31. F. L. Hirshfeld, *Theor. Chim. Acta* **1977,** *44*, 129-138.

S32. A. V. Marenich, S. V. Jerome, C. J. Cramer, D. G. Truhlar, *J. Chem. Theory Comput.* **2012,** *8*, 527-541.

S33. K. B. Wiberg, *Tetrahedron* **1968,** *24*, 1083-1096.

S34. I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270-274.

S35. A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1985,** *83*, 1736-1740.

S36. NBO 5.G. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001, http://www.chem.wisc.edu/~nbo5.

S37. A. V. Marenich, C. J. Cramer, D. G. Truhlar, CM5PAC, version 2011; Department of Chemistry, University of Minnesota: Minneapolis, MN, 2011.

Cartesian Coordinates (Å) of all DFT-optimized Structures:

Geometry of complex: [(H2-N,N'-dppz)Pt(TFE)2]4+

53
Stoichiometry = H18C22F6N4O2Pt

C	-0.959931	-3.296374	-1.435223
C	-2.202664	-2.723723	-1.168819
C	-2.263981	-1.424210	-0.602519
C	-1.043158	-0.765092	-0.338647
C	0.220700	-2.583820	-1.156500
C	-3.477930	-0.701321	-0.265672
C	-0.989447	0.527328	0.272604
C	-2.152590	1.240746	0.636542
C	-3.423382	0.605179	0.336481
C	-1.982850	2.504392	1.261418
H	-2.819706	3.120836	1.571837
C	-0.695839	2.981414	1.501594
C	0.424741	2.219779	1.118369
H	-0.886212	-4.289087	-1.858294
H	-3.088887	-3.304431	-1.401049
H	1.199765	-3.000135	-1.347772
H	-0.536849	3.936848	1.983208
H	1.435185	2.564965	1.292146
Pt	1.764884	-0.170202	-0.161497
N	0.176235	-1.337728	-0.624775
N	0.273700	1.021211	0.505103
O	3.255531	-1.523236	-0.958115
H	3.555932	-1.398125	-1.880829
O	3.349170	1.143615	0.435099
H	3.851406	0.864851	1.229690
C	-5.919336	-0.625018	-0.234320
C	-5.864576	0.699842	0.372854
N	-4.714464	-1.228831	-0.509267
N	-4.613091	1.217796	0.613588
C	-7.159172	-1.228907	-0.516095
C	-7.051084	1.390738	0.682129
C	-8.320828	-0.530411	-0.203367
C	-8.266896	0.777912	0.395440
H	-9.287413	-0.974097	-0.410772
H	-7.215364	-2.213623	-0.965628
H	-9.193982	1.290120	0.624662
H	-7.025782	2.376473	1.132321
H	-4.766632	-2.155541	-0.936939
C	4.127819	2.042065	-0.457549
C	3.182932	3.152245	-0.888712
H	4.480168	1.488391	-1.327983
F	1.990046	2.561717	-1.403641
F	2.769531	3.918337	0.201720
F	3.725397	3.947363	-1.837949
H	4.967706	2.453907	0.102855
C	4.180772	-2.423249	-0.206545
C	3.620996	-2.547243	1.197964
H	5.182886	-1.992825	-0.178420
H	4.192378	-3.398015	-0.695855
F	2.263262	-2.919340	1.154322
F	3.637004	-1.272662	1.834133
F	4.312792	-3.420659	1.952708
H	-4.587890	2.148592	1.035013

Geometry of complex: [(dppz)Pt(H2SO4)(TFE)]2+

49
Stoichiometry = H15C20F3N4O5Pt

C	0.978747	3.264809	0.412402
C	2.279121	2.772789	0.288619
C	2.482223	1.379345	0.164840
C	1.349404	0.548824	0.160410
C	-0.120178	2.387087	0.400952
C	3.792724	0.753405	0.048349
C	1.458866	-0.869058	0.070689
C	2.704464	-1.510273	-0.027914
C	3.903550	-0.683198	-0.049925
C	2.713296	-2.922662	-0.095238
H	3.666653	-3.431686	-0.171929
C	1.502877	-3.616717	-0.060020
C	0.284935	-2.920115	0.037447
H	0.791192	4.324075	0.522011
H	3.144154	3.424922	0.292201
H	-1.137990	2.738457	0.512357
H	1.479338	-4.696583	-0.107657
H	-0.672307	-3.421972	0.065045
Pt	-1.344055	-0.377592	0.205626
N	0.069607	1.052550	0.265185
N	0.272077	-1.568521	0.101496
O	-3.022336	0.944981	0.260405
H	-3.668753	0.883296	0.997061
O	-2.770277	-2.026267	0.204134
C	6.100138	0.946829	-0.075461
C	6.211622	-0.503872	-0.178135
N	4.877856	1.550853	0.037137
N	5.097058	-1.297001	-0.160694
C	7.276744	1.741096	-0.095758
C	7.495633	-1.098039	-0.298070
C	8.512691	1.128718	-0.214338
C	8.622128	-0.293085	-0.316251
H	9.413759	1.729116	-0.231402
H	7.173967	2.815955	-0.018555
H	9.604095	-0.740288	-0.409321
H	7.559693	-2.176009	-0.373180
C	-3.551246	1.670923	-0.908726
C	-4.185642	2.949051	-0.382238
H	-4.292325	1.064562	-1.434047
F	-5.113680	2.595446	0.619760
F	-3.236183	3.770814	0.226220
F	-4.826584	3.648785	-1.362935
H	-2.704339	1.888950	-1.556561
S	-4.204852	-1.975570	-0.239848
O	-4.574917	-1.356201	-1.497971
O	-4.756292	-3.452939	-0.245123
O	-4.917889	-1.252524	1.015531
H	-5.905255	-1.197217	0.982867
H	-4.505056	-4.056407	0.495016

Geometry of complex: [(dppz)Pt(HSO4)(TFE)]+

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```
Stoichiometry = H14C20F3N4O5Pt
   C      0.896965    3.251621    0.475547
   C      2.200176    2.771511    0.339359
   C      2.410179    1.382387    0.193373
   C      1.284263    0.543977    0.179448
   C     -0.193181    2.362986    0.454374
   C      3.728359    0.771374    0.062585
   C      1.410218   -0.877392    0.068885
   C      2.661140   -1.503044   -0.042931
   C      3.853454   -0.663256   -0.058665
   C      2.688150   -2.913321   -0.126683
   H      3.647600   -3.408399   -0.214718
   C      1.487514   -3.623503   -0.091258
   C      0.261064   -2.943278    0.020234
   H      0.701863    4.307758    0.601640
   H      3.061345    3.428364    0.349366
   H     -1.215854    2.698883    0.575644
   H      1.477141   -4.703103   -0.149570
   H     -0.698316   -3.443485    0.050962
   Pt    -1.399983   -0.436050    0.218720
   N     -0.000085    1.032922    0.296058
   N      0.234751   -1.593539    0.096325
   O     -3.076738    0.877836    0.337397
   H     -3.848162    0.411216    0.787288
   O     -2.622053   -2.122357    0.210910
   C      6.034637    0.986494   -0.066339
   C      6.159683   -0.455225   -0.192864
   N      4.806661    1.578329    0.060337
   N      5.053271   -1.261652   -0.183834
   C      7.204381    1.792941   -0.077518
   C      7.449853   -1.034991   -0.327497
   C      8.446192    1.196968   -0.210489
   C      8.569122   -0.221048   -0.336479
   H      9.340982    1.807489   -0.220744
   H      7.088434    2.865369    0.017901
   H      9.554856   -0.658285   -0.440463
   H      7.520909   -2.111459   -0.420523
   C     -3.534971    1.582559   -0.865673
   C     -4.163586    2.886609   -0.413492
   H     -4.254482    0.969012   -1.412725
   F     -5.195628    2.656983    0.492859
   F     -3.225623    3.707573    0.235138
   F     -4.664427    3.593606   -1.488965
   H     -2.663553    1.784719   -1.486805
   S     -4.107400   -2.066088   -0.270803
   O     -4.225831   -1.285029   -1.512507
   O     -4.750097   -3.363143   -0.074978
   O     -4.757960   -0.999294    0.883814
   H     -5.347041   -1.424949    1.541332


Geometry of complex: [(dppz)Pt(TFE)2]2+
----------------------------------------

51
Stoichiometry = H16C22F6N4O2Pt
   C     -1.075865   -3.275409   -1.460406
   C     -2.309467   -2.681124   -1.188781
   C     -2.343492   -1.388984   -0.618191
   C     -1.116827   -0.754220   -0.357876
   C      0.118271   -2.590409   -1.179787
```

C	-3.570399	-0.680128	-0.280232
C	-1.053885	0.535265	0.245527
C	-2.213524	1.245237	0.597051
C	-3.506037	0.631633	0.320336
C	-2.053075	2.511788	1.204752
H	-2.938369	3.074059	1.475741
C	-0.766594	2.996176	1.442550
C	0.359095	2.237748	1.074905
H	-1.017543	-4.267444	-1.886539
H	-3.246961	-3.183277	-1.395382
H	1.089131	-3.027837	-1.367024
H	-0.608978	3.957689	1.911003
H	1.367174	2.584903	1.249524
Pt	1.671433	-0.187504	-0.167167
N	0.094244	-1.346680	-0.645316
N	0.210468	1.032776	0.479245
O	3.193588	-1.541221	-0.960127
H	3.359498	-1.535585	-1.921341
O	3.283418	1.107745	0.449257
H	3.726477	0.870229	1.286926
C	-5.886999	-0.602799	-0.219276
C	-5.822166	0.723827	0.383813
N	-4.745370	-1.284080	-0.541448
N	-4.617854	1.318064	0.645401
C	-7.153161	-1.192474	-0.475258
C	-7.026460	1.405617	0.701740
C	-8.307095	-0.499404	-0.152834
C	-8.243706	0.801844	0.436351
H	-9.276126	-0.943151	-0.345327
H	-7.181643	-2.178792	-0.920743
H	-9.165848	1.316962	0.676235
H	-6.958403	2.389884	1.147302
C	4.109801	1.933112	-0.442025
C	3.286721	3.149975	-0.834786
H	4.367172	1.361716	-1.334027
F	2.070196	2.746477	-1.409578
F	2.965908	3.922843	0.280179
F	3.964707	3.924520	-1.738775
H	5.010111	2.251999	0.082609
C	4.077891	-2.488649	-0.256384
C	3.625454	-2.562171	1.189971
H	5.110477	-2.138701	-0.297048
H	3.989569	-3.478173	-0.707981
F	2.279933	-2.909614	1.288916
F	3.764777	-1.302409	1.822801
F	4.379495	-3.464111	1.880891

Geometry of complex: anti-[(H-+N-dppz)Pt(H2SO4)(TFE)]3+

50
Stoichiometry = H16C20F3N4O5Pt

C	1.050031	3.095073	1.185714
C	2.308054	2.534261	0.968582
C	2.390573	1.195273	0.520741
C	1.198733	0.487923	0.312034
C	-0.116785	2.338286	0.960605
C	3.647255	0.504680	0.257003
C	1.197059	-0.870623	-0.125779
C	2.387703	-1.580917	-0.394221

C	3.633035	-0.855220	-0.202836
C	2.258942	-2.928102	-0.815657
H	3.122565	-3.543540	-1.041921
C	0.992106	-3.495679	-0.945555
C	-0.156343	-2.735659	-0.663911
H	0.945473	4.115166	1.528853
H	3.218074	3.097241	1.134984
H	-1.105006	2.749638	1.115032
H	0.875846	-4.522284	-1.263566
H	-1.155951	-3.138983	-0.754395
Pt	-1.569447	-0.186439	0.145797
N	-0.036597	1.059347	0.529240
N	-0.047213	-1.447550	-0.263767
O	-3.083830	1.260852	0.593123
H	-3.617433	1.085251	1.397400
O	-3.097419	-1.663834	-0.301387
C	5.986115	0.595181	0.223401
C	6.056022	-0.778488	-0.261146
N	4.793489	1.192410	0.462304
N	4.849074	-1.427259	-0.443951
C	7.197269	1.310673	0.441654
C	7.292985	-1.391549	-0.518160
C	8.407727	0.691573	0.187693
C	8.453611	-0.655552	-0.292936
H	9.336297	1.223110	0.349738
H	7.133325	2.328684	0.802273
H	9.416592	-1.112815	-0.484277
H	7.350889	-2.411449	-0.880828
C	-3.886536	1.931346	-0.457395
C	-3.003694	3.014432	-1.055713
H	-4.768701	2.377321	0.002088
F	-2.627640	3.949368	-0.093092
F	-1.801227	2.439868	-1.528783
F	-3.626199	3.646439	-2.089054
H	-4.171393	1.211390	-1.226539
S	-4.402631	-1.836776	0.439960
O	-4.767730	-0.835151	1.430685
O	-5.572025	-1.871901	-0.618039
O	-4.263646	-3.311549	1.002360
H	-4.950498	-3.624110	1.644259
H	4.891542	-2.388170	-0.778788
H	-5.564308	-2.544286	-1.342927

Geometry of complex: anti-[(H-+N-dppz)Pt(HSO4)(TFE)]2+

49
Stoichiometry = H15C20F3N4O5Pt

C	0.905374	3.166306	1.170547
C	2.175132	2.625390	0.968769
C	2.282506	1.301459	0.486800
C	1.101670	0.590895	0.227157
C	-0.245393	2.401102	0.898343
C	3.552482	0.628371	0.243849
C	1.127561	-0.756732	-0.258256
C	2.331347	-1.451354	-0.501767
C	3.559325	-0.726410	-0.245610
C	2.233684	-2.787845	-0.964647
H	3.112675	-3.389056	-1.171874
C	0.978971	-3.359741	-1.160592

C	-0.185428	-2.613731	-0.904599
H	0.783246	4.175220	1.539343
H	3.074425	3.192156	1.173920
H	-1.245365	2.788111	1.047300
H	0.880585	-4.378152	-1.508597
H	-1.180410	-3.015001	-1.044864
Pt	-1.661466	-0.148480	-0.015321
N	-0.145435	1.136198	0.431018
N	-0.102073	-1.337001	-0.463727
O	-3.323726	1.040548	0.577750
H	-3.872711	0.395623	1.132249
O	-3.152118	-1.485756	-0.522077
C	5.892783	0.715645	0.278746
C	5.981034	-0.645098	-0.217495
N	4.690160	1.310871	0.493147
N	4.782557	-1.291895	-0.452125
C	7.095187	1.429602	0.540700
C	7.227126	-1.256552	-0.439854
C	8.314731	0.815921	0.318448
C	8.379003	-0.524552	-0.171283
H	9.235707	1.348901	0.514869
H	7.016292	2.443373	0.910178
H	9.347501	-0.980012	-0.335613
H	7.292968	-2.273286	-0.810327
C	-4.154203	1.660659	-0.467188
C	-3.422838	2.906929	-0.923821
H	-5.112246	1.943224	-0.030577
F	-3.182516	3.784826	0.135355
F	-2.149069	2.580051	-1.442100
F	-4.124086	3.568445	-1.896716
H	-4.298412	0.973529	-1.304269
S	-3.716081	-2.407341	0.617853
O	-4.841779	-3.191281	0.126087
O	-2.617690	-3.011770	1.391994
O	-4.340692	-1.137177	1.570724
H	-4.862266	-1.443083	2.344340
H	4.831978	-2.247834	-0.799068

Geometry of complex: syn-[(H-+N-dppz)Pt(H2SO4)(TFE)]3+

50
Stoichiometry = H16C20F3N4O5Pt

C	0.972188	3.153975	1.179979
C	2.242767	2.620453	0.973369
C	2.378618	1.278638	0.536916
C	1.193274	0.540505	0.328027
C	-0.171796	2.367925	0.955887
C	3.628789	0.584601	0.275559
C	1.205836	-0.819436	-0.106485
C	2.402479	-1.501380	-0.365643
C	3.654523	-0.778686	-0.174220
C	2.326437	-2.846716	-0.795432
H	3.239309	-3.390636	-1.004213
C	1.072161	-3.440062	-0.940295
C	-0.098561	-2.707280	-0.664598
H	0.844960	4.174338	1.513556
H	3.102557	3.255941	1.154954
H	-1.171575	2.754073	1.102434
H	0.978184	-4.466841	-1.266044

H	-1.087004	-3.134252	-0.767324
Pt	-1.567422	-0.188402	0.146392
N	-0.054305	1.087868	0.534431
N	-0.026058	-1.419491	-0.256638
O	-3.119755	1.228608	0.591618
H	-3.658782	1.029312	1.386777
O	-3.058377	-1.686250	-0.316232
C	6.052437	0.572335	0.197864
C	5.993047	-0.809530	-0.264623
N	4.840460	1.191140	0.441292
N	4.805012	-1.439761	-0.433156
C	7.284556	1.221198	0.378599
C	7.209323	-1.496743	-0.537054
C	8.450718	0.511898	0.101964
C	8.414871	-0.843333	-0.355816
H	9.410092	0.996390	0.235516
H	7.334433	2.247743	0.723212
H	9.347192	-1.353706	-0.559002
H	7.153634	-2.521161	-0.880374
C	-3.931689	1.878322	-0.464317
C	-3.070043	2.981223	-1.056360
H	-4.827470	2.304036	-0.011952
F	-2.714768	3.920663	-0.087931
F	-1.851808	2.434736	-1.524679
F	-3.698933	3.605265	-2.089405
H	-4.193958	1.151465	-1.235112
S	-4.355862	-1.908651	0.426170
O	-4.766040	-0.911103	1.403617
O	-5.518109	-2.008878	-0.634644
O	-4.152107	-3.368381	1.007124
H	-4.827971	-3.707586	1.647211
H	4.875374	2.157364	0.761590
H	-5.476920	-2.686349	-1.353690

Geometry of complex: syn-[(H-+N-dppz)Pt(HSO4)(TFE)]2+

49

Stoichiometry = H15C20F3N4O5Pt

C	0.839953	3.193581	1.182662
C	2.118815	2.676317	0.989625
C	2.271546	1.350686	0.510901
C	1.097408	0.614619	0.243316
C	-0.290663	2.403893	0.905225
C	3.530118	0.675150	0.265933
C	1.135989	-0.731426	-0.245591
C	2.345308	-1.397019	-0.490428
C	3.584671	-0.674693	-0.234376
C	2.293603	-2.727318	-0.964035
H	3.216348	-3.259173	-1.158393
C	1.049123	-3.323272	-1.167205
C	-0.134502	-2.605875	-0.907130
H	0.697765	4.201103	1.547093
H	2.971943	3.308293	1.212877
H	-1.300212	2.768607	1.047741
H	0.970993	-4.340626	-1.524304
H	-1.118965	-3.030100	-1.052499
Pt	-1.658653	-0.163542	-0.012352
N	-0.159025	1.140394	0.439843
N	-0.083533	-1.331814	-0.456114

O	-3.337902	1.018757	0.561750
H	-3.890048	0.369203	1.110222
O	-3.132214	-1.510311	-0.521541
C	5.953820	0.685578	0.276643
C	5.926544	-0.669523	-0.240580
N	4.728028	1.284083	0.497985
N	4.751055	-1.309003	-0.477259
C	7.172189	1.339231	0.531132
C	7.159128	-1.332626	-0.495833
C	8.355372	0.655437	0.271161
C	8.350714	-0.677147	-0.243519
H	9.303129	1.143550	0.461373
H	7.193760	2.351400	0.918942
H	9.294519	-1.171374	-0.432691
H	7.124271	-2.342768	-0.881706
C	-4.159171	1.624915	-0.497851
C	-3.436128	2.879059	-0.945238
H	-5.128060	1.896986	-0.078617
F	-3.217624	3.758823	0.119213
F	-2.149974	2.568719	-1.445203
F	-4.129149	3.535693	-1.926053
H	-4.281725	0.934026	-1.335385
S	-3.711713	-2.427753	0.615460
O	-4.824228	-3.218305	0.105129
O	-2.628819	-3.017608	1.419505
O	-4.364254	-1.150598	1.545350
H	-4.896069	-1.453782	2.312915
H	4.736016	2.237396	0.855322

Geometry of complex: [(H-+N-dppz)Pt(TFE)2]3+

52
Stoichiometry = H17C22F6N4O2Pt

C	-0.985057	-3.306242	-1.470180
C	-2.228241	-2.736706	-1.199646
C	-2.298034	-1.441979	-0.629636
C	-1.077647	-0.781747	-0.365020
C	0.192907	-2.595132	-1.188254
C	-3.514207	-0.723857	-0.286583
C	-1.025132	0.509776	0.238677
C	-2.188280	1.210269	0.586886
C	-3.474203	0.583108	0.304949
C	-2.051146	2.479730	1.195673
H	-2.938129	3.039538	1.464800
C	-0.770458	2.973734	1.440077
C	0.364144	2.222834	1.075451
H	-0.909877	-4.296054	-1.897937
H	-3.117478	-3.311822	-1.432355
H	1.171939	-3.009970	-1.381237
H	-0.622966	3.935771	1.910986
H	1.367328	2.581854	1.256234
Pt	1.718161	-0.178366	-0.171410
N	0.143763	-1.353810	-0.651630
N	0.234079	1.018737	0.475061
O	3.236116	-1.531365	-0.949354
H	3.501874	-1.444268	-1.885304
O	3.303490	1.131971	0.442513
H	3.761550	0.887205	1.271840
C	-5.933721	-0.602327	-0.203570

C	-5.809579	0.726790	0.386570
N	-4.753107	-1.252340	-0.508259
N	-4.592462	1.273709	0.624180
C	-7.194915	-1.171467	-0.442693
C	-6.992487	1.447555	0.713167
C	-8.326523	-0.432721	-0.106955
C	-8.227442	0.874317	0.468358
H	-9.307574	-0.855983	-0.284059
H	-7.293687	-2.159252	-0.877878
H	-9.134700	1.411423	0.711985
H	-6.888671	2.432439	1.148457
H	-4.835347	-2.178661	-0.923374
C	4.106640	2.007398	-0.435751
C	3.220962	3.175338	-0.840456
H	4.417315	1.453861	-1.321878
F	2.024396	2.682649	-1.410872
F	2.838137	3.926492	0.270275
F	3.842022	3.980302	-1.745541
H	4.974470	2.369699	0.115105
C	4.155717	-2.427050	-0.205613
C	3.637346	-2.529907	1.216633
H	5.164959	-2.012445	-0.202085
H	4.147028	-3.413484	-0.671212
F	2.288453	-2.905953	1.235638
F	3.695791	-1.262681	1.853584
F	4.366618	-3.409315	1.945209

Geometry of complex: [(H-+N-dppz)Pt(TFE)2]3+.HSO4-

58
Stoichiometry = H18C22F6N4O6Pt

C	0.674767	-3.412443	-0.033138
C	1.861524	-2.765204	-0.389059
C	1.827647	-1.378465	-0.656355
C	0.587407	-0.726030	-0.612012
C	-0.522002	-2.693735	0.058428
C	2.985338	-0.536600	-0.877677
C	0.450423	0.653120	-0.945306
C	1.542595	1.435956	-1.346824
C	2.867286	0.831827	-1.283402
C	1.302100	2.775025	-1.721513
H	2.136902	3.395302	-2.023294
C	-0.004301	3.265039	-1.684163
C	-1.058533	2.443752	-1.248617
H	0.669494	-4.470023	0.188561
H	2.781546	-3.329376	-0.452177
H	-1.453724	-3.163117	0.342331
H	-0.228735	4.282069	-1.973729
H	-2.076078	2.802274	-1.186378
Pt	-2.142252	-0.133018	-0.086766
N	-0.561742	-1.368747	-0.232135
N	-0.826190	1.165292	-0.874710
O	-3.447578	-1.577342	0.898301
H	-3.275830	-1.760300	1.841461
O	-3.772868	1.271654	0.009555
H	-4.477583	1.156202	-0.656845
C	5.358193	-0.252854	-0.798763
C	5.185228	1.089342	-1.321916
N	4.229320	-1.012183	-0.623979

N	3.941776	1.611423	-1.518762
C	6.634235	-0.738709	-0.452970
C	6.338708	1.887955	-1.550943
C	7.734078	0.075525	-0.679535
C	7.588494	1.382899	-1.240186
H	8.724576	-0.281538	-0.426030
H	6.741365	-1.725400	-0.018785
H	8.472818	1.984571	-1.407111
H	6.201974	2.883998	-1.950761
H	4.265545	-1.818143	0.055310
C	-4.218971	1.972227	1.221873
C	-3.244792	3.110434	1.481044
H	-4.208471	1.283569	2.066998
F	-1.937019	2.615538	1.595780
F	-3.234898	4.017890	0.420249
F	-3.570565	3.773004	2.634563
H	-5.219657	2.374524	1.065740
C	-4.563809	-2.383290	0.373060
C	-4.595536	-2.202119	-1.132470
H	-5.506165	-2.040940	0.802462
H	-4.397547	-3.437428	0.602343
F	-3.378037	-2.545274	-1.715745
F	-4.833207	-0.845124	-1.467286
F	-5.591518	-2.950332	-1.686343
O	1.955088	-0.477906	1.870883
S	3.221410	-1.060938	2.425582
O	3.682604	-2.240167	1.580820
O	4.392758	0.073470	2.018020
H	4.692884	0.579235	2.803115
O	3.284291	-1.265814	3.877924

Geometry of complex: [(phen)Pt(H2SO4)(TFE)]2+

39

Stoichiometry = H13C14F3N2O5Pt

C	-2.546747	-2.913190	1.233329
C	-3.766003	-2.294014	0.971946
C	-3.783455	-0.962375	0.476970
C	-2.534475	-0.335830	0.270339
C	-1.332608	-2.232371	1.004311
C	-2.453090	0.993380	-0.199866
C	-3.619599	1.738071	-0.483775
C	-3.437552	3.071687	-0.939515
H	-4.298289	3.686085	-1.174641
C	-2.149005	3.581738	-1.078801
C	-1.025884	2.784027	-0.776826
H	-2.504218	-3.924316	1.613491
H	-4.697160	-2.819757	1.146644
H	-0.373601	-2.693231	1.196622
H	-1.986117	4.594256	-1.421106
H	-0.013482	3.151649	-0.875867
Pt	0.259158	0.186074	0.116605
N	-1.334298	-0.971087	0.527880
N	-1.182029	1.513988	-0.348415
O	1.713943	-1.310080	0.647193
H	2.219009	-1.151191	1.470717
O	1.892701	1.548718	-0.386771
C	2.511709	-2.037795	-0.357868
C	1.619959	-3.132260	-0.920675

H	3.383438	-2.480140	0.124002
F	1.218561	-4.019399	0.076971
F	0.443813	-2.574376	-1.452178
F	2.264144	-3.826786	-1.908707
H	2.814414	-1.356808	-1.155186
S	3.142123	1.752764	0.423193
O	3.499376	0.777214	1.443357
O	4.365325	1.825159	-0.578076
O	2.945802	3.229327	0.978411
H	3.593902	3.544773	1.655844
C	-4.969126	-0.202140	0.177541
H	-5.935468	-0.669122	0.325337
C	-4.891163	1.092357	-0.284324
H	-5.795097	1.648168	-0.502905
H	4.305091	2.425994	-1.359875

Geometry of complex: [(phen)Pt(HSO4)(TFE)]1+

38

Stoichiometry = H12C14F3N2O5Pt

C	-1.572273	-3.671900	0.327393
C	-2.933661	-3.441768	0.151152
C	-3.403166	-2.109475	-0.000516
C	-2.436579	-1.079056	0.022481
C	-0.660088	-2.595406	0.343126
C	-2.820603	0.280237	-0.091033
C	-4.176579	0.644931	-0.240032
C	-4.465020	2.033065	-0.333403
H	-5.490145	2.364810	-0.450175
C	-3.426456	2.957802	-0.271467
C	-2.090997	2.527404	-0.117497
H	-1.188308	-4.674085	0.458570
H	-3.634831	-4.267995	0.138278
H	0.401544	-2.744100	0.498351
H	-3.621424	4.019137	-0.339120
H	-1.251075	3.207942	-0.061388
Pt	0.012743	0.383275	0.170212
N	-1.084925	-1.325788	0.180140
N	-1.804896	1.213298	-0.030718
O	1.892214	-0.598006	0.379405
H	2.532341	-0.003900	0.882394
O	0.881815	2.270277	0.239502
C	2.550252	-1.177652	-0.797525
C	3.354936	-2.373483	-0.325486
H	3.195795	-0.436290	-1.273276
F	4.256761	-2.010074	0.671160
F	2.522747	-3.366506	0.221090
F	4.053805	-2.943009	-1.370901
H	1.774529	-1.499282	-1.490948
S	2.381606	2.503890	-0.137114
O	2.725702	1.787160	-1.374878
O	2.753447	3.892775	0.118055
O	3.141942	1.550330	1.049494
H	3.592629	2.063302	1.752514
C	-4.783207	-1.731172	-0.163115
H	-5.534186	-2.512459	-0.188785
C	-5.154764	-0.411045	-0.278128
H	-6.199314	-0.146217	-0.395568

Geometry of complex: [(phen)Pt(TFE)]2+

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Stoichiometry = H14C16F6N2O2Pt

C	-2.756303	-2.900370	-1.478304
C	-3.898834	-2.179424	-1.139255
C	-3.766772	-0.913243	-0.509377
C	-2.453436	-0.447696	-0.269716
C	-1.475970	-2.375133	-1.212378
C	-4.860941	-0.077132	-0.088422
C	-2.225671	0.784788	0.380159
C	-3.301940	1.595905	0.803899
C	-4.637660	1.126613	0.540545
C	-2.975783	2.810899	1.464903
H	-3.764063	3.471724	1.805329
C	-1.639735	3.139137	1.676921
C	-0.611867	2.281445	1.233726
H	-2.830880	-3.871161	-1.948229
H	-4.883024	-2.582581	-1.345976
H	-0.575373	-2.919469	-1.461256
H	-1.362657	4.052996	2.183745
H	0.432003	2.514210	1.389594
Pt	0.386603	-0.211312	-0.161961
N	-1.329080	-1.167392	-0.628668
N	-0.905471	1.132775	0.591122
O	1.731862	-1.677735	-1.065091
H	1.876200	-1.632653	-2.028993
O	2.140099	0.890507	0.446920
H	2.611529	0.516706	1.217885
C	3.016551	1.657576	-0.452537
C	2.289013	2.944292	-0.808356
H	3.212304	1.083414	-1.358698
F	1.024598	2.652591	-1.351284
F	2.064830	3.728615	0.321441
F	3.004088	3.667500	-1.724445
H	3.948377	1.893721	0.061120
C	2.484426	-2.790189	-0.452086
C	2.138867	-2.827591	1.024429
H	3.555762	-2.624331	-0.572245
H	2.187582	-3.734770	-0.911189
F	0.767971	-2.986225	1.222501
F	2.498786	-1.609137	1.654085
F	2.807196	-3.836456	1.649115
H	-5.873514	-0.416459	-0.271534
H	-5.473984	1.739873	0.853988