Electronic Supplementary Information

Hemilabile Bonding of 1-oxa-4,7-dithiacyclononane in Cyclometallated Palladium(II) Complexes

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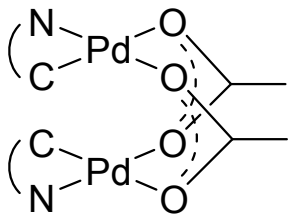
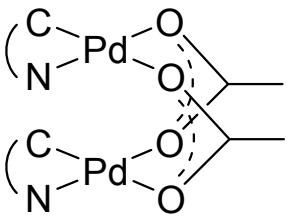
Scheme S1. ***anti*** **and** ***syn*** **isomers of** $[Pd(C\hat{}N)(\mu^2\text{-}O_2CCH_3)]_2$



anti isomer



syn isomer

Table S1. Crystal Data, Data Collection, and Refinement Parameters for $[Pd(fpp)(\mu\text{-}O_2CCH_3)]_2$ (6a), $[Pd(ppyCHO)(\mu\text{-}O_2CCH_3)]_2$ (2a), and $[Pd(ppyCHO)([9]aneS_3)](PF_6)$ (2c)

Compound	**6a**	**2a**	**2c**
Formula	$C_{28}H_{20}F_6N_2O_4Pd_2$	$C_{28}H_{22}N_2O_6Pd_2$	$C_{18}H_{20}F_6NOPPdS_3$
Lattice type	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P-1
a, Å	24.572(2)	9.9503(17)	6.826(2)
b, Å	9.7149(8)	10.8027(18)	10.590(4)
c, Å	23.534(2)	13.062(2)	15.068(5)
α, deg	90	87.421(6)	84.736(6)
β, deg	105.282(10)	71.412(5)	85.891(6)
γ, deg	90	68.718(5)	79.079(6)
V, Å^3	5419.4(9)	1236.0(4)	1063.4(6)
Z	8	2	2
Fwt., g mol^{-1}	775.27	695.29	613.91
D_c, Mg m^{-3}	1.900	1.868	1.917
Total refls.	26969	12973	7477
Unique refls.	6210 (R_{int}=0.033)	5641 (R_{int}=0.033)	4775 (R_{int}=0.017)
Data, rest., param.	6210 / 6 / 385	5641 / 0 / 345	4775 / 0 / 280
R_1, wR_2 ($I > 2\sigma(I)$)	0.0487, 0.0959	0.0342, 0.0768	0.0271, 0.0676
R_1, wR_2 (all data)	0.0623 / 0.1018	0.0465, 0.0817	0.0314, 0.0690
Goodness-of-fit (F^2)	1.100	1.040	1.096

Table S2 Calculated Atomic Charges (a.u.) for Pd coordination sphere of *endo*-**4b** and *exo*-**4b** using NBO and CHELPG Methods

***endo*-4b**			***exo*-4b**		
	CHELPG	NBO		CHELPG	NBO
Pd1	0.32359	0.51739	Pd1	0.32430	0.50195
S1	-0.11866	0.34565	S1	-0.07925	0.33578
S2	-0.16802	0.26970	S2	-0.16959	0.27069
O1	-0.51527	-0.61233	O1	-0.46687	-0.63421
N1	-0.29790	-0.48601	N1	-0.24469	-0.48358
C19	-0.39208	-0.11667	C19	-0.35623	-0.11595

Table S3. Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis for Calculated *endo*-4b, *exo*-4b, and [Pd(btp)(9[ane]S_3)]$^+$ Structures

***endo*-4b**

Donor NBO (i)	Acceptor NBO (j)	E(2)(kcal/mol)	e(j)-e(i) (a.u.)	F(i,j) (a.u.)
Lone pair (1) O4	Lone valence Pd1	2.04	0.54	0.03
Lone pair (1) O4	Lone valence Pd1	1.08	0.36	0.018

***exo*-4b**

Donor NBO (i)	Acceptor NBO (j)	E(2)(kcal/mol)	e(j)-e(i) (a.u.)	F(i,j) (a.u.)
No O4….Pd1 interactions found above 0.5 kcal/mol threshold				

[Pd(btp)(9[ane]S_3)]$^+$

Donor NBO (i)	Acceptor NBO (j)	E(2)(kcal/mol)	e(j)-e(i) (a.u.)	F(i,j) (a.u.)
Lone pair (2) S4	Lone valence Pd1	8.53	0.29	0.045
Lone pair (1) S4	Lone valence Pd1	2.79	0.53	0.034

$$E(2) = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

q_i is the donor orbital occupancy, e_i, e_j are diagonal elements (orbital energies)

F(i,j) is the off-diagonal NBO Fock matrix element

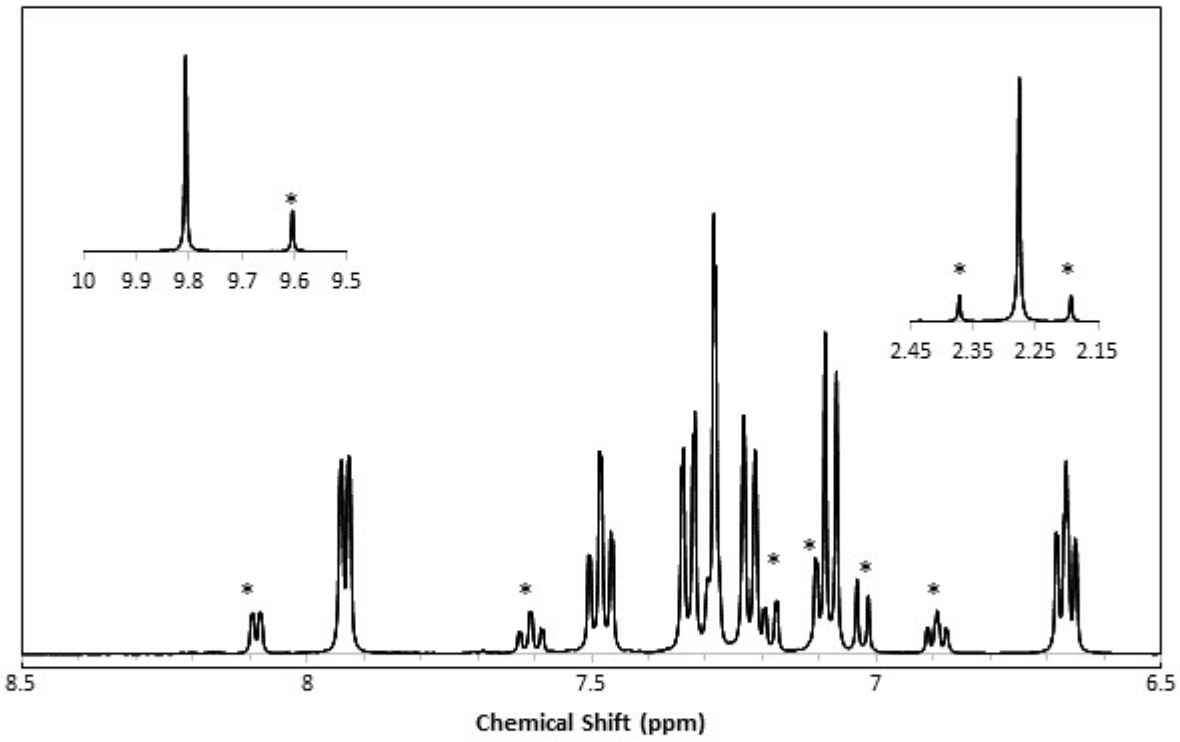


Figure S1. ^{1}H NMR spectrum of [Pd(ppyCHO)(μ-O_2CCH_3)]$_2$ (**2a**) in CD_2Cl_2. Insets show downfield aldehyde region (upper left) and acetate aliphatic region (upper right). * indicates minor *syn* isomer peaks.

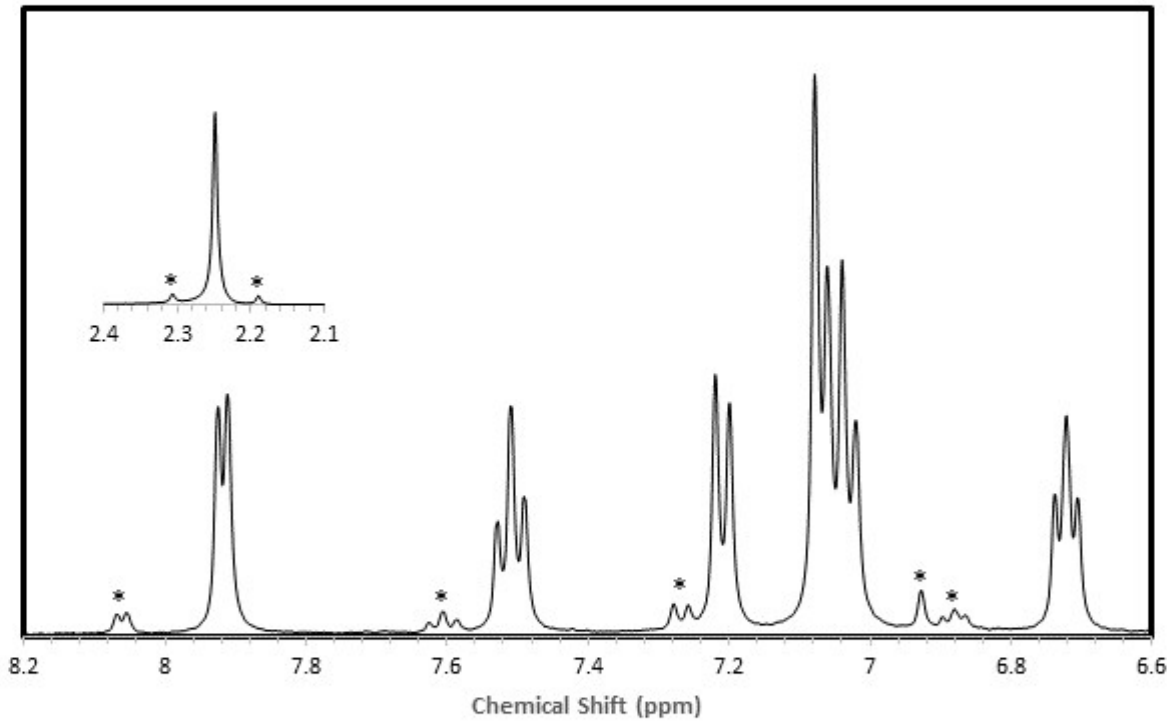


Figure S2. ^{1}H NMR spectrum of $[Pd(fpp)(\mu\text{-}O_2CCH_3)]_2$ (**6a**) in CD_2Cl_2. Insets show downfield aldehyde region (upper left) and acetate aliphatic region (upper right). * indicates minor *syn* isomer peaks.

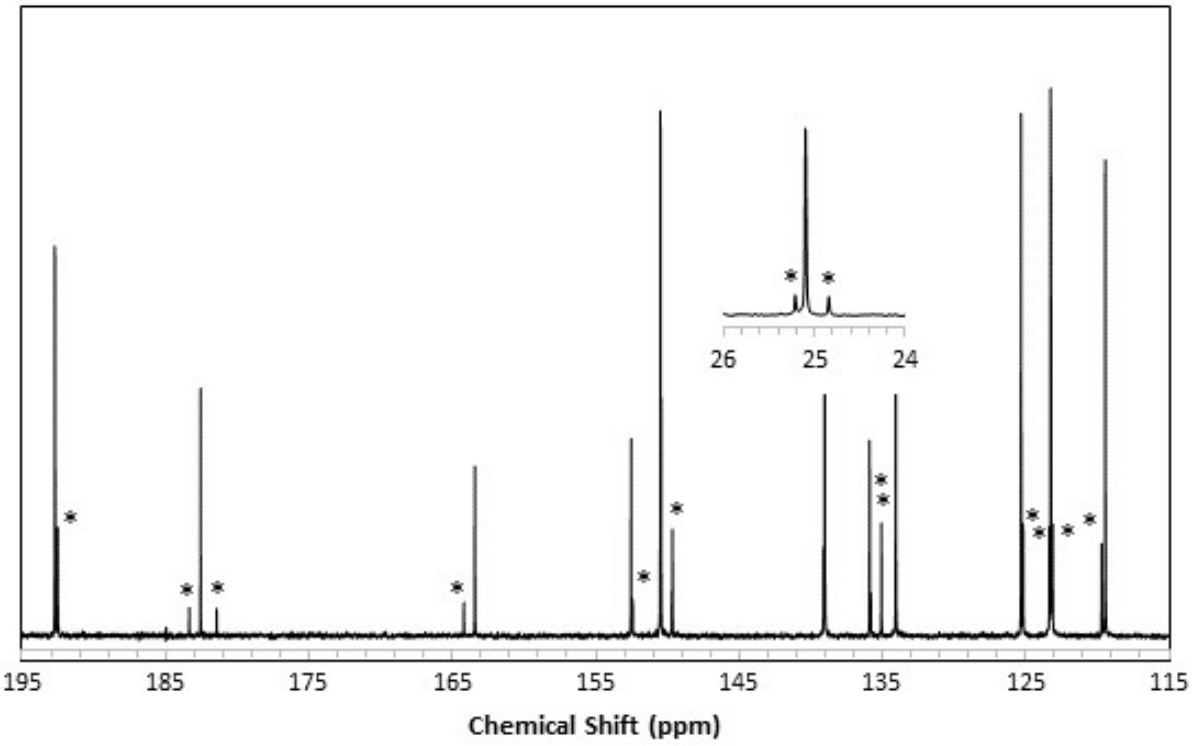


Figure S3 ^{13}C NMR spectrum of $[Pd(ppyCHO)(\mu\text{-}O_2CCH_3)]_2$ (**2a**) in CD_2Cl_2. Inset shows the upfield acetate aliphatic region. * indicates minor *syn* isomer peaks.

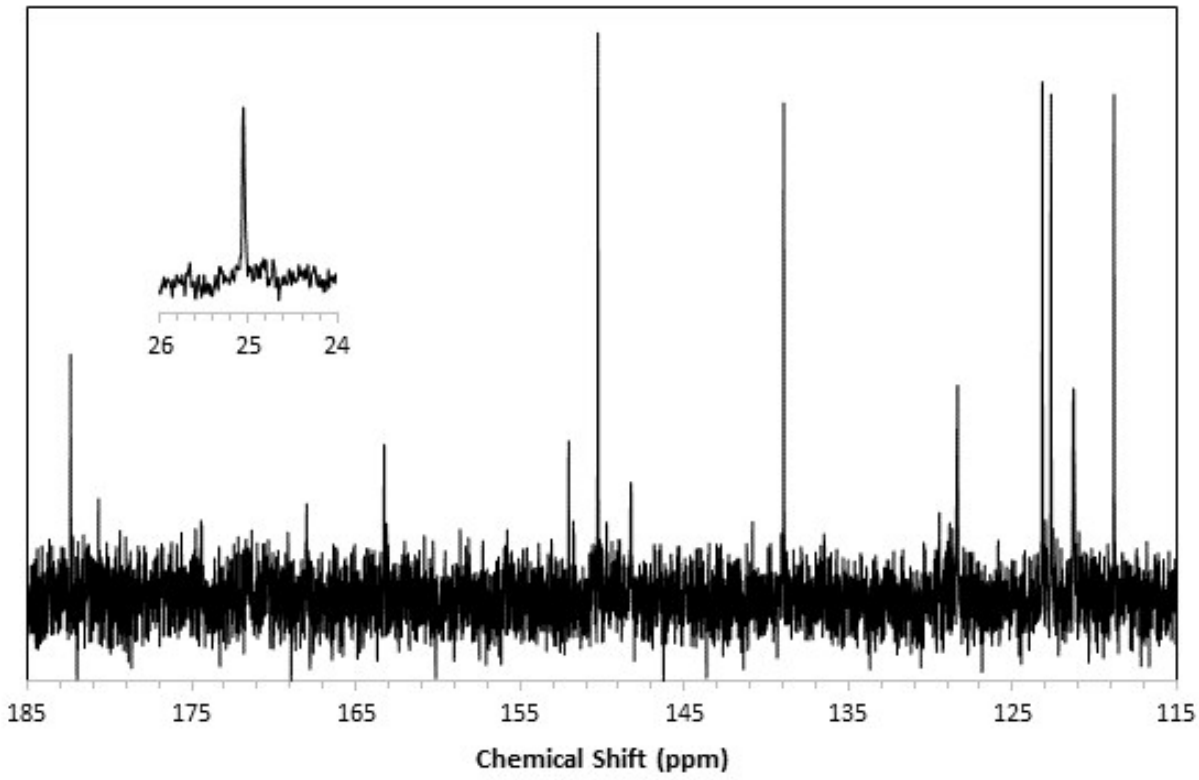


Figure S4 ^{13}C NMR spectrum of $[Pd(fpp)(\mu\text{-}O_2CCH_3)]_2$ (**6a**) in CD_2Cl_2. Inset shows the upfield acetate aliphatic region. Signal-to noise ratio (precluded by solubility) and ratio of *anti/syn* is too large to resolve the *syn* isomer peaks.

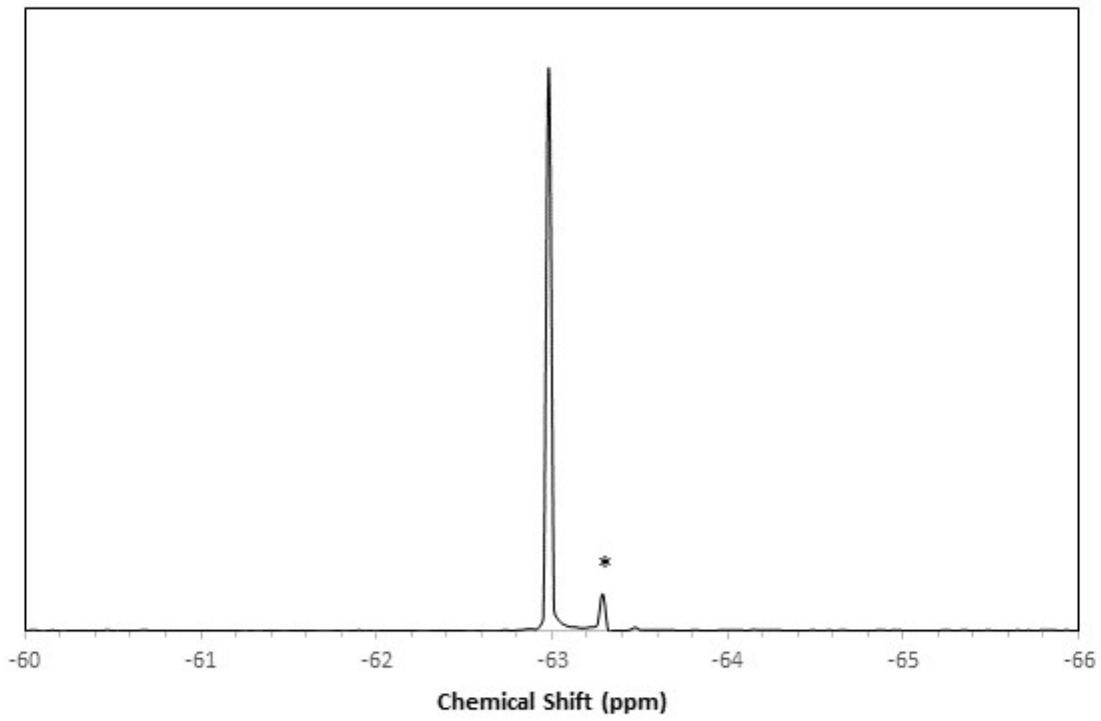


Figure S5 ^{19}F NMR spectrum of $[Pd(fpp)(\mu\text{-}O_2CCH_3)]_2$ (**6a**) in CD_2Cl_2. Inset shows the upfield acetate aliphatic region. * indicates minor *syn* isomer.

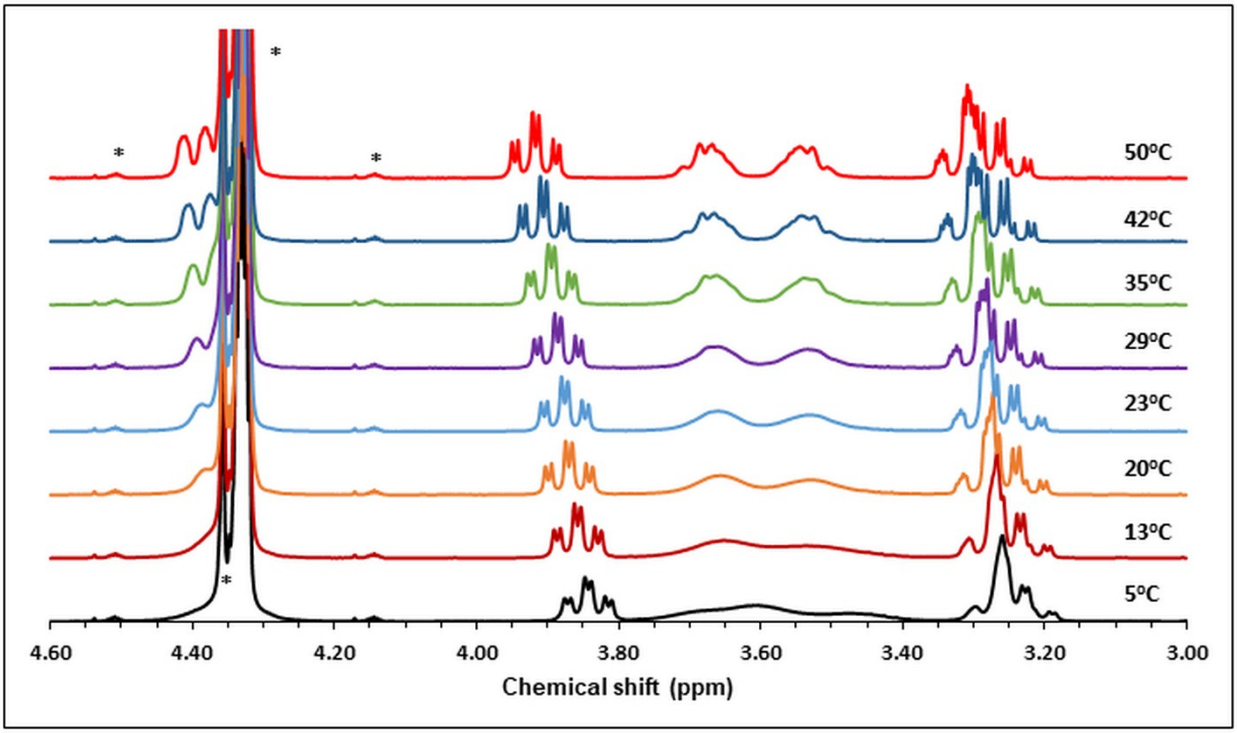


Figure S6. Variable Temperature ^{1}H NMR of [Pd(pbt)([9]aneS_2O)](PF_6) (**5b**), in CD_3NO_2, aliphatic region. * indicates peaks associated with residual CD_2HNO_2 or CH_3NO_2 (solvent of recrystallization)

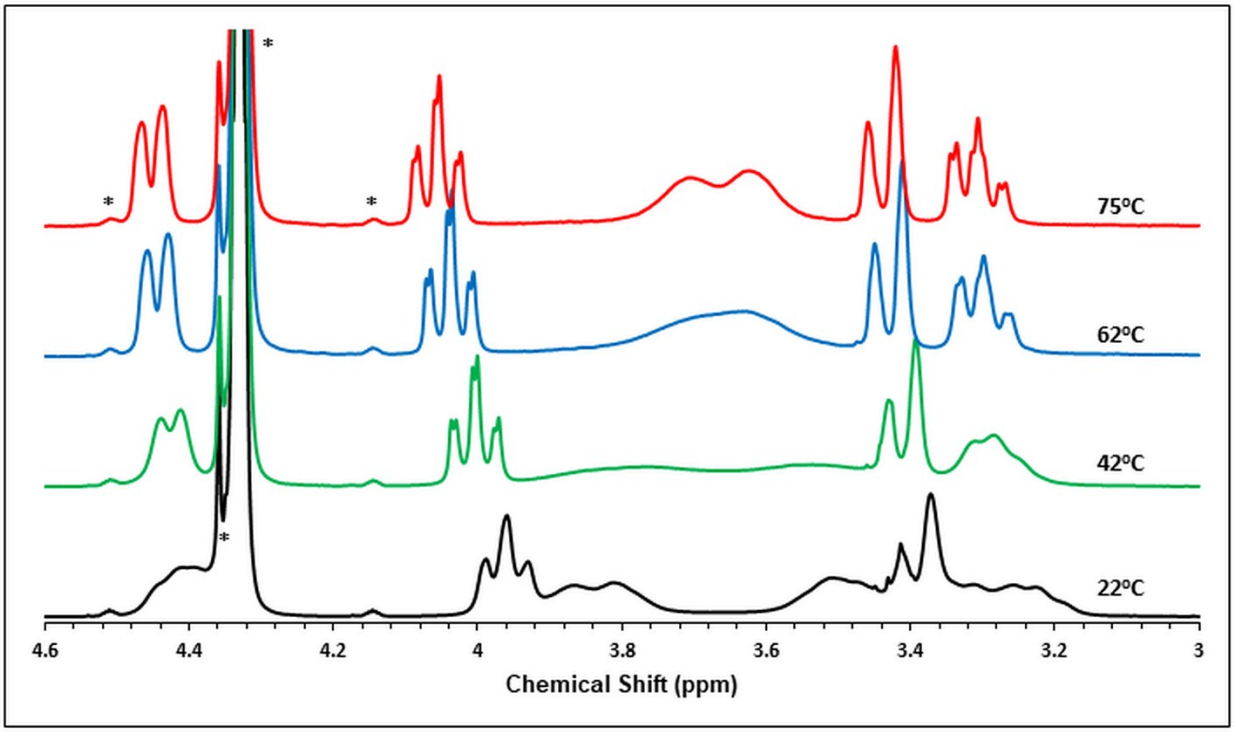


Figure S7. Variable Temperature ^{1}H NMR of [Pd(bzq)([9]aneS_2O)](PF_6) (**3b**), in CD_3NO_2, aliphatic region. * indicates peaks associated with residual CD_2HNO_2 or CH_3NO_2 (solvent of recrystallization)

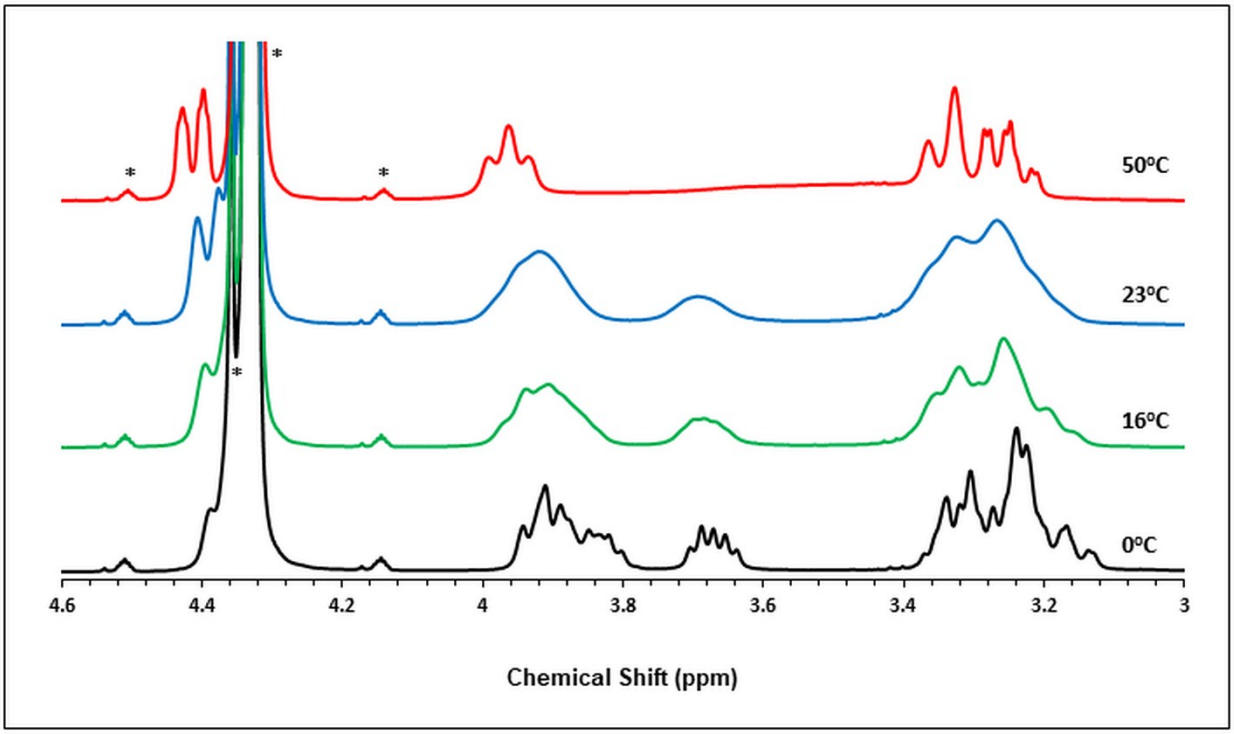


Figure S8. Variable Temperature ^{1}H NMR of [Pd(btp)([9]aneS_2O)](PF_6) (**4b**), in CD_3NO_2, aliphatic region. * indicates peaks associated with residual CD_2HNO_2 or CH_3NO_2 (solvent of recrystallization)

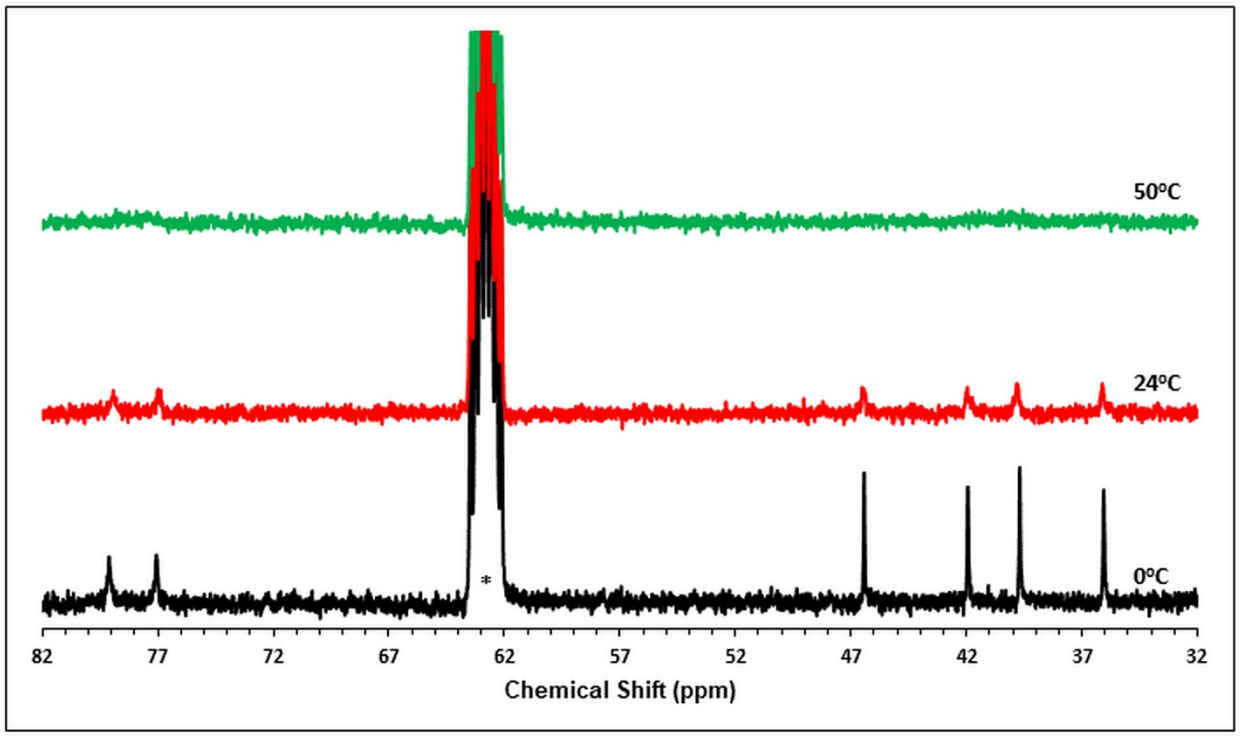


Figure S9. Variable Temperature ^{13}C NMR of [Pd(btp)([9]aneS_2O)](PF_6) (**4b**), in CD_3NO_2, aliphatic region. Each spectrum was collected using 3000 scans and the vertical scales are plotted identically. * indicates peaks associated with residual CD_2HNO_2.

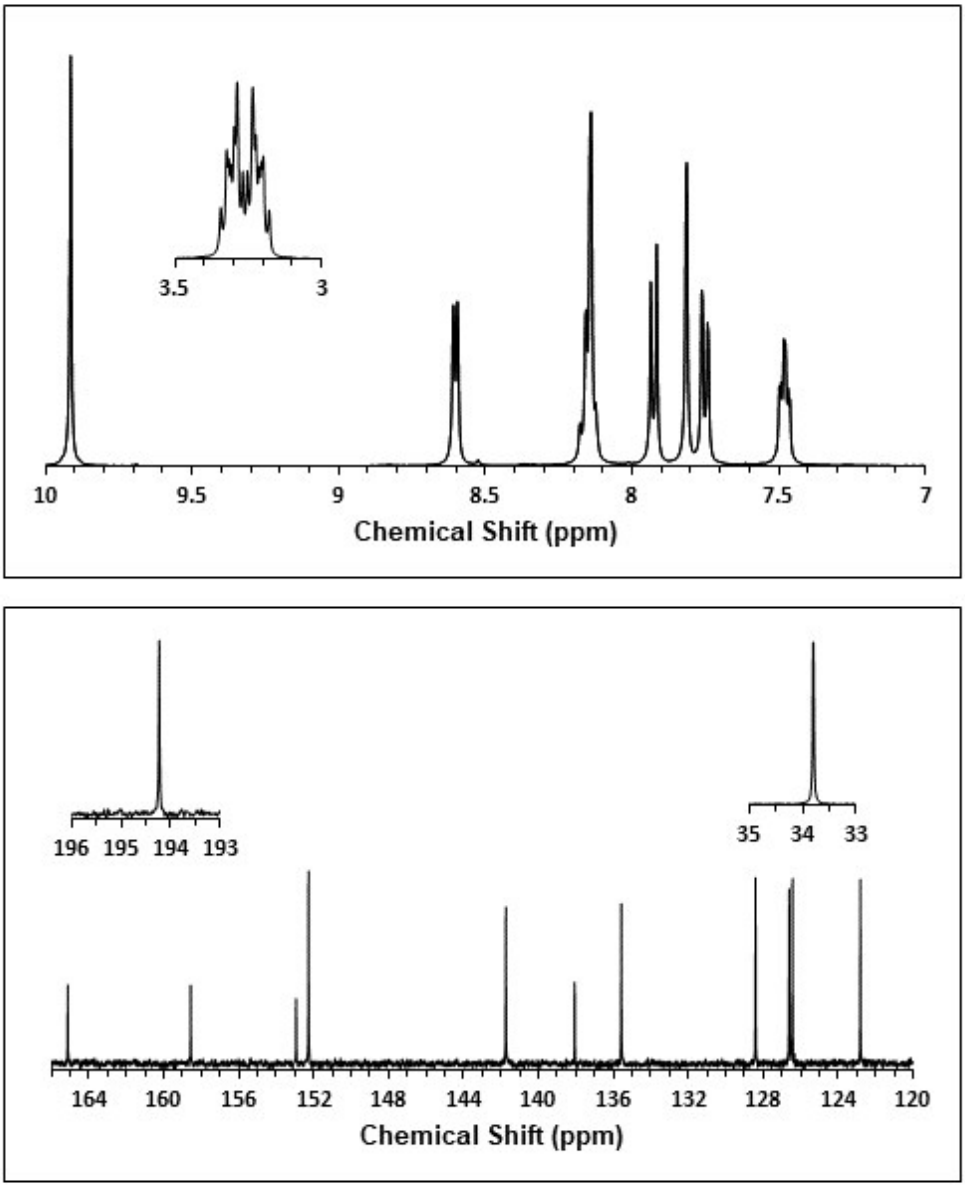


Figure S10. ^{1}H and ^{13}C NMR spectra of [Pd(ppyCHO)([9]aneS_3)](PF_6) (**2c**) in CD_3NO_2. Above: ^{1}H NMR, inset shows upfield [9]aneS_3 region (upper left). Below: ^{13}C NMR, insets shows downfield aldehyde region (upper left) and upfield [9]aneS_3 region (upper right).

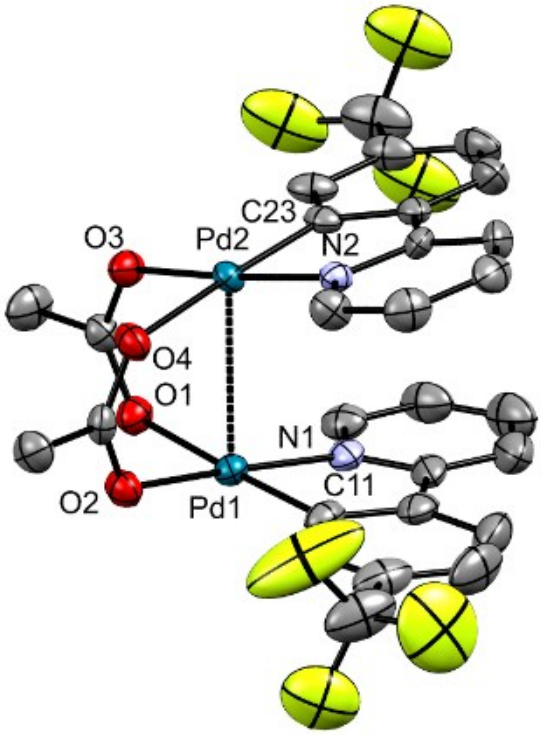


Figure S11. Thermal ellipsoid perspective of [Pd(fpp)(μ-O_2CCH_3)]$_2$ (**6a**) (50% probability, H atoms omitted for clarity).

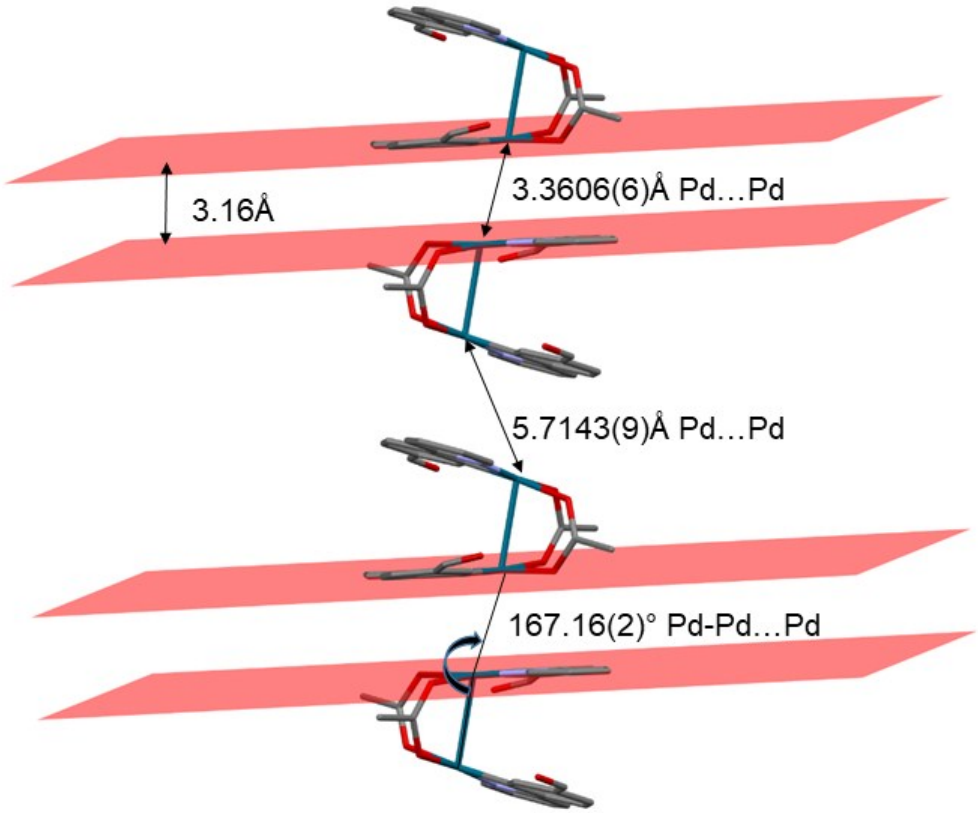


Figure S12. Packing diagram of $[Pd(ppyCHO)(\mu\text{-}O_2CCH_3)]_2$ (**2a**) (H atoms omitted for clarity).

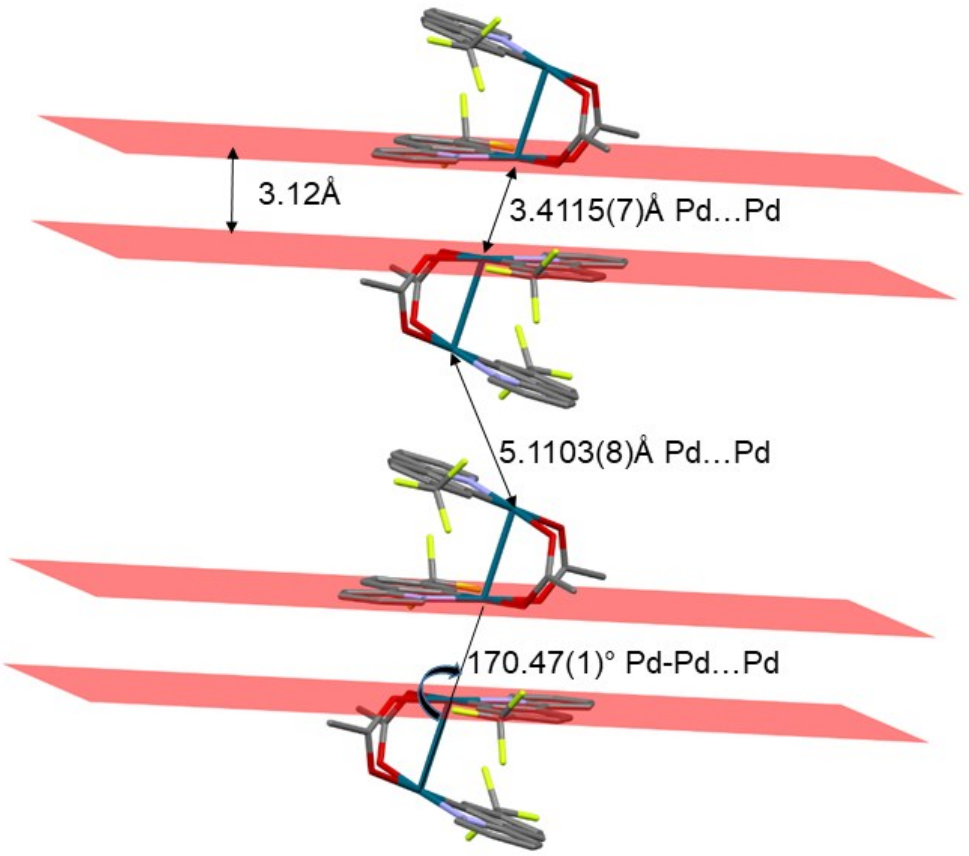


Figure S13. Packing diagram of [Pd(fpp)(μ-O_2CCH_3)]$_2$ (**6a**) (H atoms omitted for clarity).

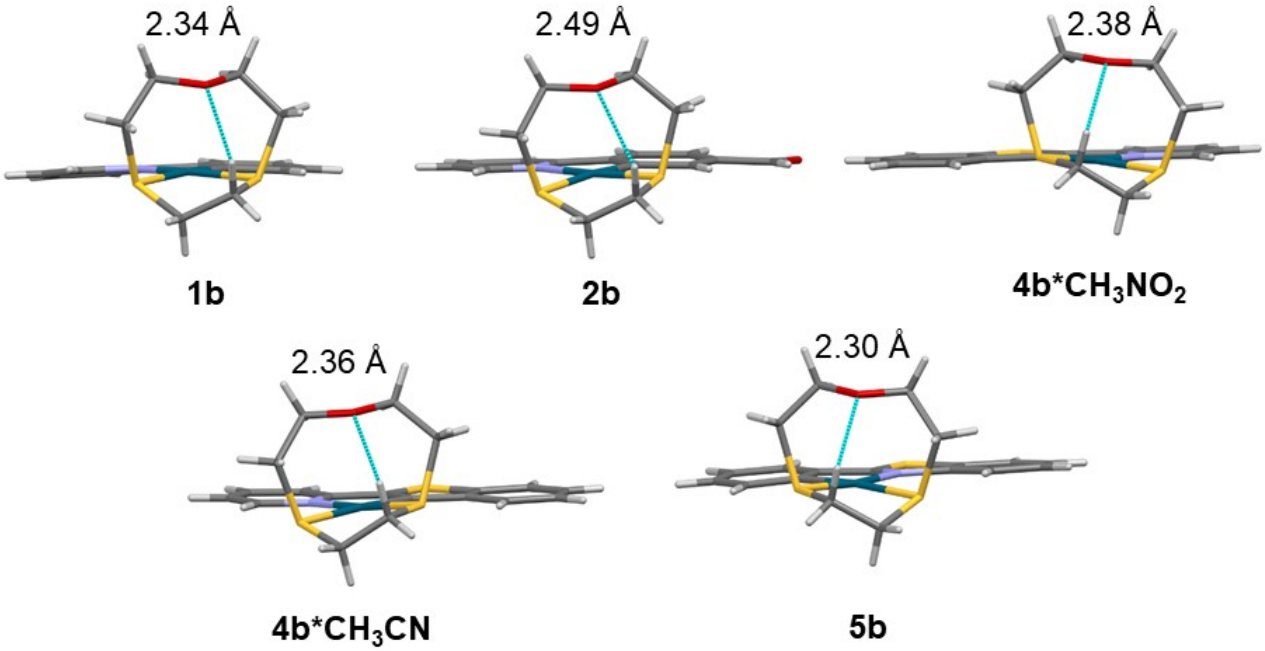


Figure S14. Short intramacrocyclic CH…O contacts in structures **1b**, **2b**, **4b*CH_3NO_2**, **4b*CH_3CN**, **5b*CH_3NO_2**. H atoms, anions, and solvent excluded for clarity.

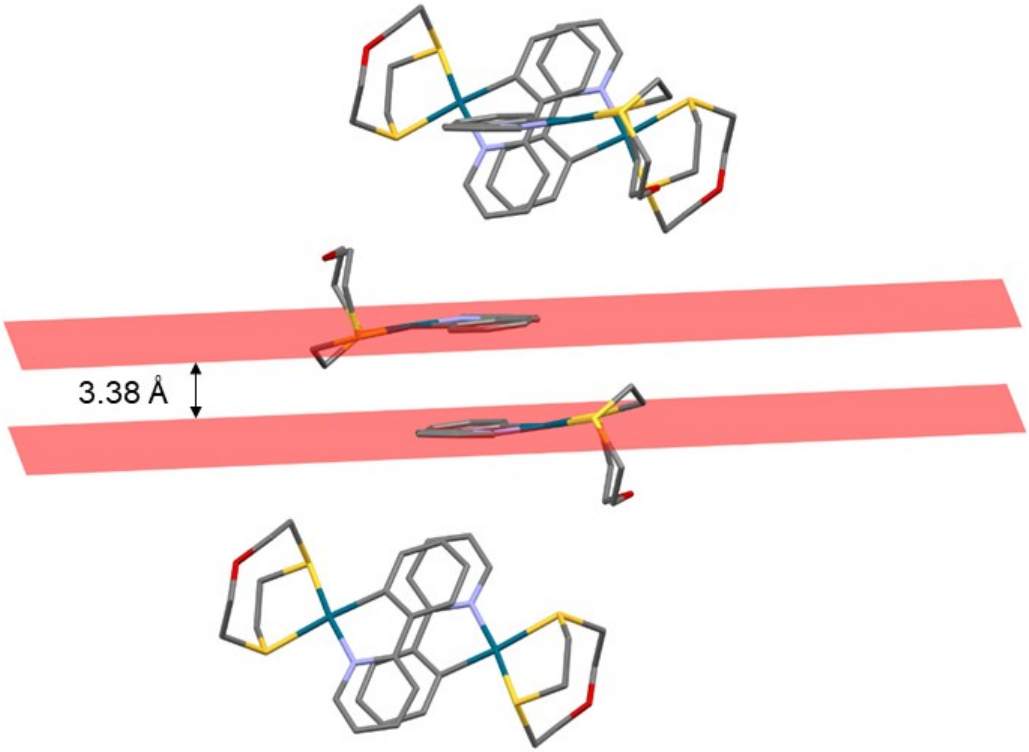


Figure S15. Intermolecular π-stacking diagram of [Pd(ppy)([9]aneS_2O)](PF_6) (**1b**) (H atoms, solvent, and anions omitted for clarity).

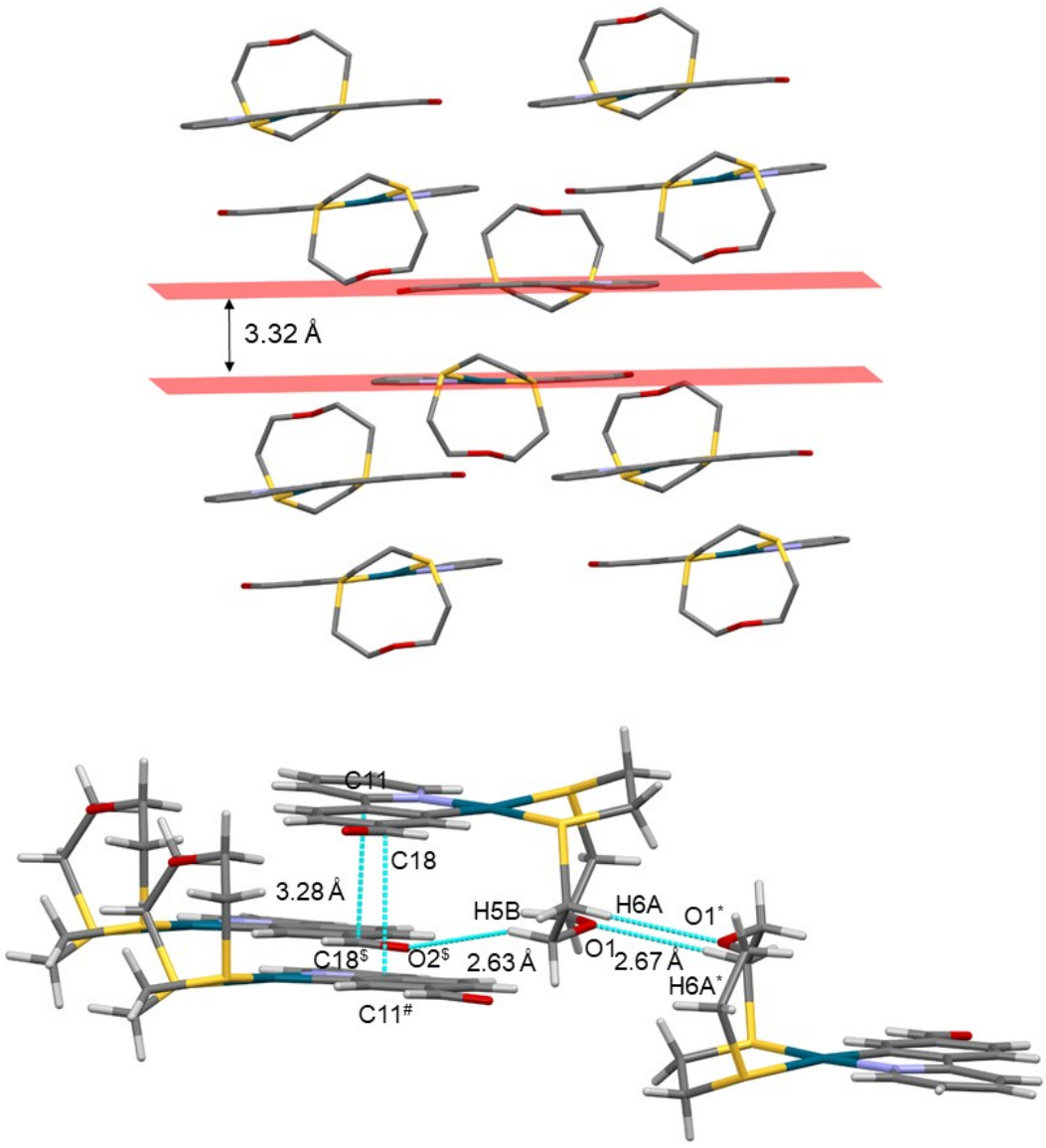


Figure S16. Intermolecular packing diagrams of [Pd(ppyCHO)([9]aneS$_2$O)](PF$_6$) (**2b**) (H atoms, solvent, and anions omitted for clarity). Above: intermolecular π-stacking diagram. Below: Close contacts details. * symmetry code: 1-x, -y, 1-z; # symmetry code: 2-x,-1/2+y,1.5-z ; $ symmetry code: 2-x,1/2+y,1.5-z.

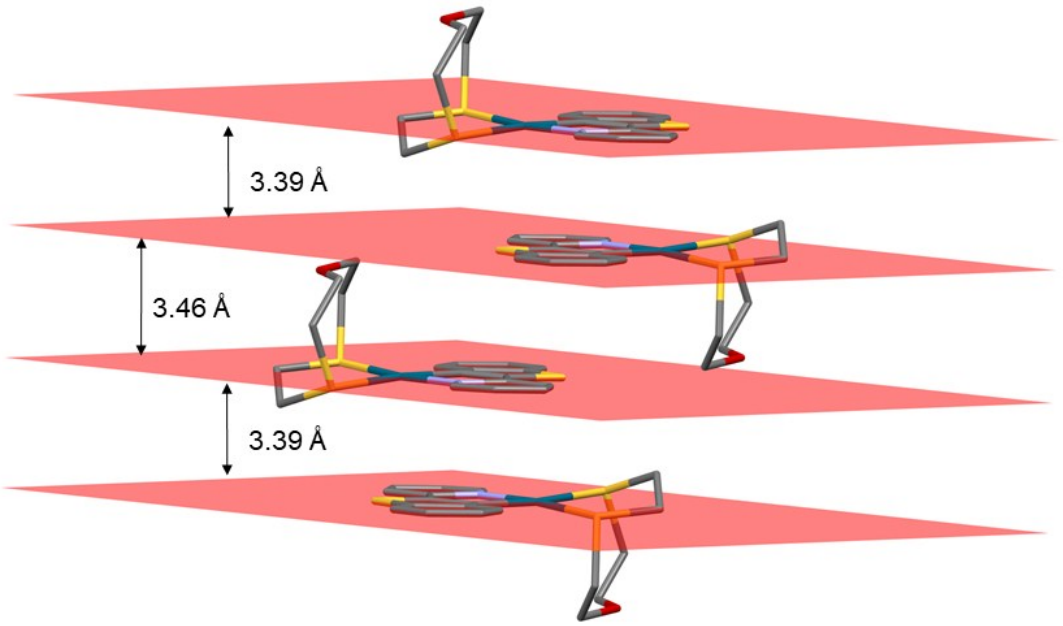


Figure S17. Intermolecular π-stacking diagram of [Pd(btp)([9]aneS$_2$O)](PF$_6$) (**4a*CH$_3$NO$_2$**) (H atoms, solvent, and anions omitted for clarity).

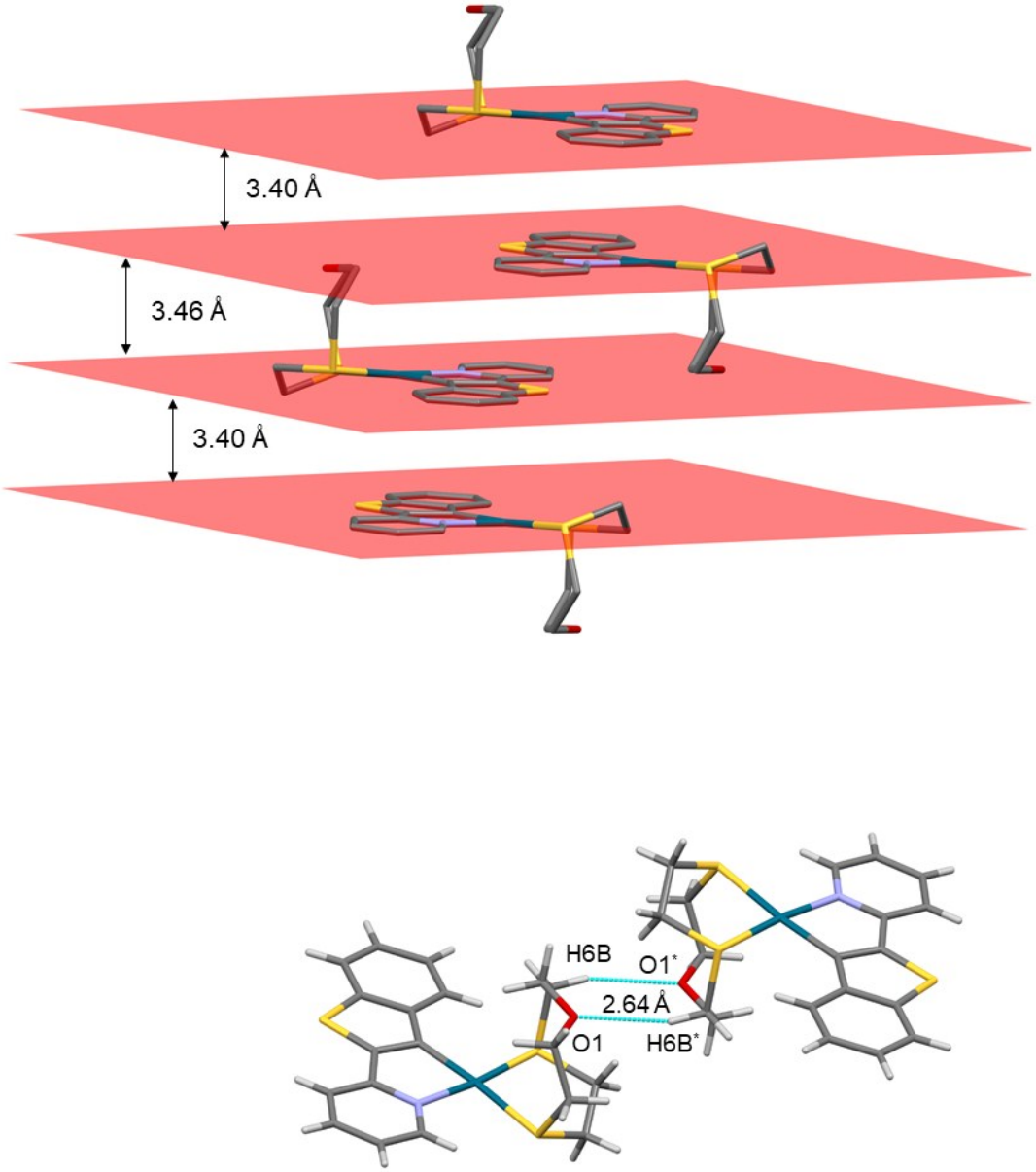


Figure S18. Intermolecular packing diagrams of [Pd(btp)([9]aneS_2O)](PF_6) (**4a*CH_3CN**) (H atoms, solvent, and anions omitted for clarity). Above: Intermolecular π-stacking diagram. Below: Details of close contacts involving [9]aneS_2O ligand. * symmetry code: -x, 2-y, 1-z

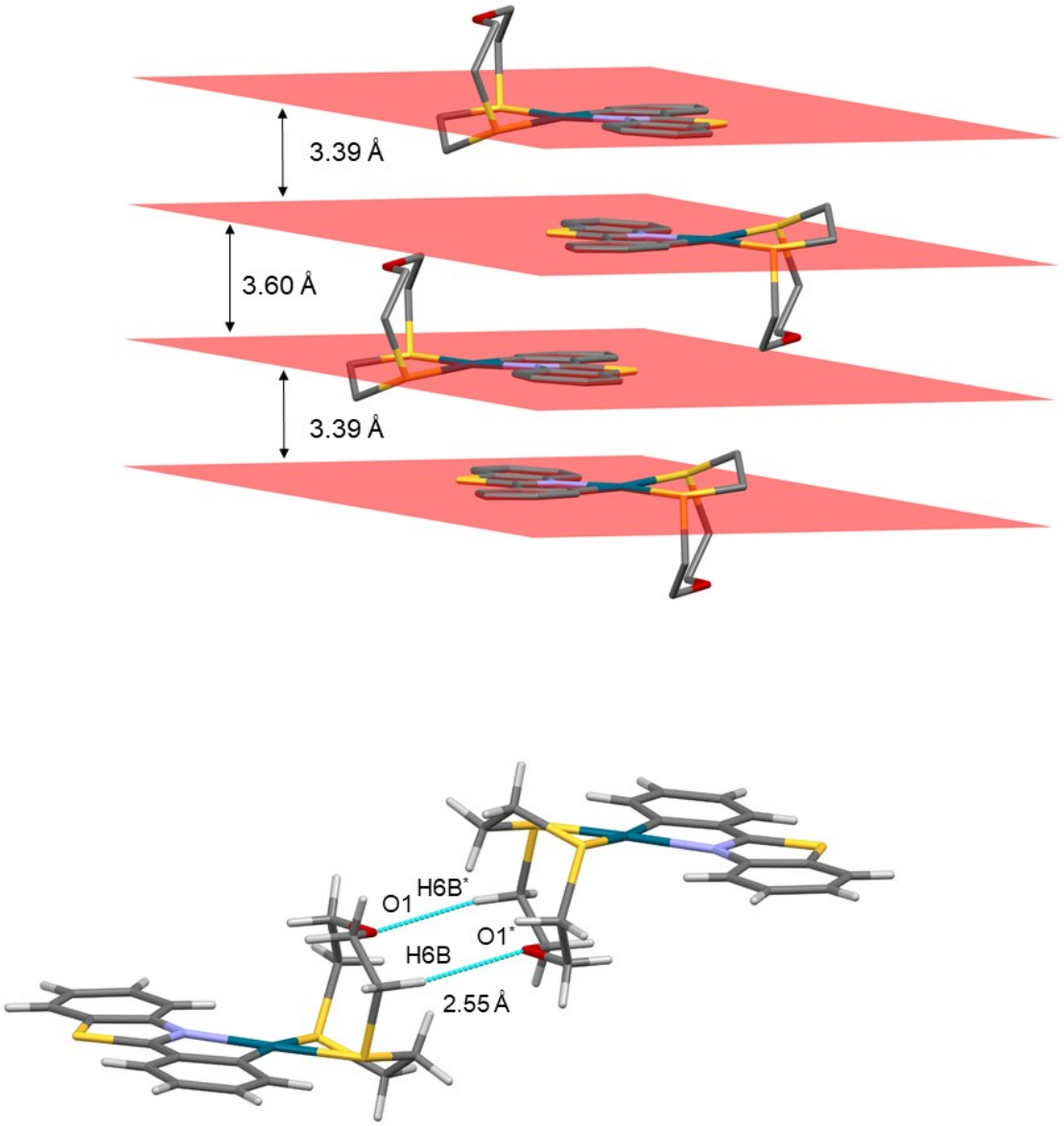


Figure S19. Intermolecular packing diagrams of [Pd(pbt)([9]aneS_2O)](PF_6) (**5b*CH_3NO_2**) (H atoms, solvent, and anions omitted for clarity). Above: Intermolecular π-stacking diagram. Below: Details of close contacts involving [9]aneS_2O ligand. * symmetry code (1-x, -y, 2-z)

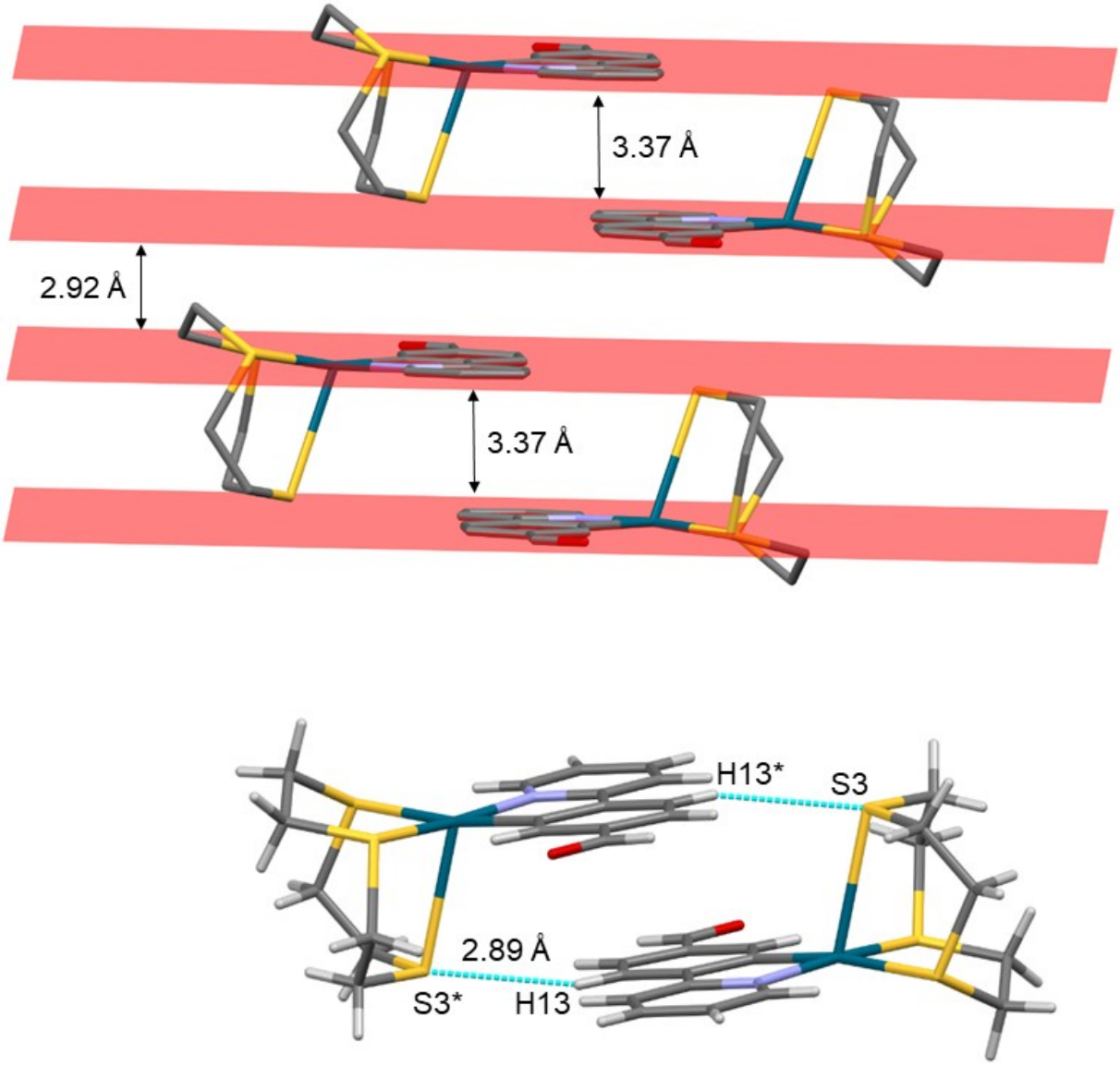


Figure S20. Intermoleclar packing diagrams of [Pd(ppyCHO)([9]aneS$_3$)](PF$_6$) (**2c)** (H atoms, solvent, and anions omitted for clarity). Above: Intermolecular π-stacking diagram. Below: Details of close contacts involving [9]aneS$_3$ ligand. * symmetry code: 2-x,-y,2-z

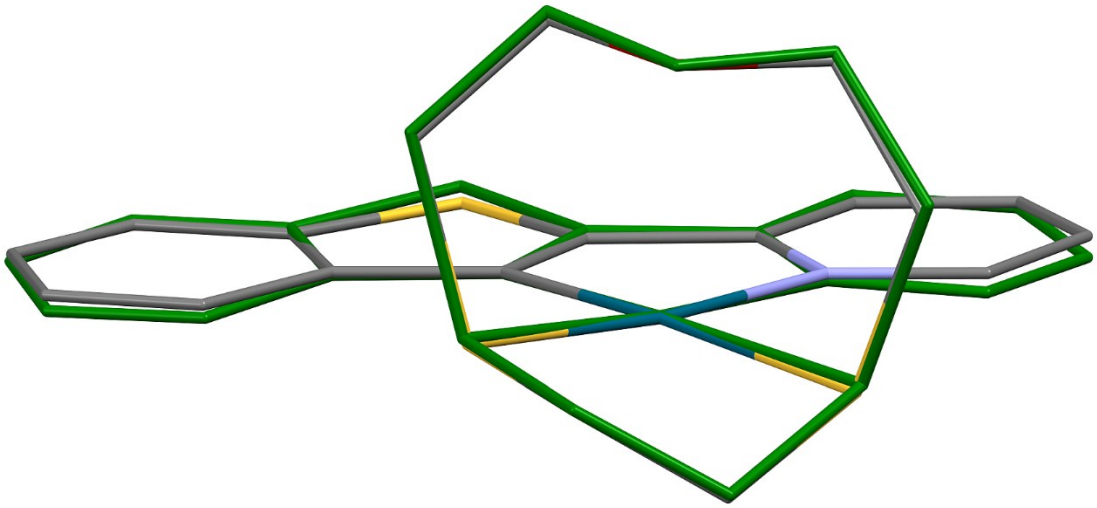


Figure S21. Overlay of experimental X-ray structure coordinates of $[Pd(btp)([9]aneS_2O)]^+$ (cation of **4b**) with DFT (including PCM with CH_3CN) calculated geometry coordinates. Tubes with color indicate experimental structure coordinates, green tubes indicate DFT calculated geometry.

Computational Details – Energies of calculated species and Cartesian Coordinates

***exo*-4b**

E(RB3LYP)	-2187.55572058 A.U.
Zero-point correction	0.352729 (Hartree/Particle)
Thermal correction to Energy	0.375893
Thermal correction to Enthalpy	0.376837
Thermal correction to Gibbs Free Energy	0.300365
Sum of electronic and zero-point Energies	-2187.202991
Sum of electronic and thermal Energies	-2187.179827
Sum of electronic and thermal Enthalpies	-2187.178883
Sum of electronic and thermal Free Energies	-2187.255356

Atom Label	X coord	Y coord	Z coord
Pd1	0.54427	0.148519	-0.431566
S1	1.025646	-2.188565	-0.508373
S2	2.970333	0.510464	-0.906346
O1	2.97317	-1.362582	1.830377
S3	-3.772168	1.164421	0.425485
N1	0.053525	2.201089	-0.232303
C1	2.812553	-2.316893	-1.019949
C2	3.308463	-1.084954	-1.749715
C3	3.996083	0.468544	0.638305
C4	3.290425	0.021756	1.909708
C5	1.674035	-1.771638	2.243314
C6	1.109986	-2.772271	1.24509
C7	0.892165	3.240972	-0.335247
C8	0.484855	4.549464	-0.109708
C9	-0.843516	4.783683	0.238211
C10	-1.719017	3.710926	0.340604
C11	-1.249939	2.41712	0.097769
C12	-2.034685	1.204578	0.127535
C13	-1.478955	-0.01882	-0.154191
C14	-2.480705	-1.062404	-0.174511
C19	-3.777346	-0.564644	0.140366
C18	-4.904445	-1.388559	0.187345
C17	-4.751225	-2.738103	-0.098765
C16	-3.489253	-3.254347	-0.437071
C15	-2.371905	-2.435298	-0.477205
H1A	3.381702	-2.497597	-0.113472
H1B	2.875074	-3.187324	-1.674557
H2A	2.827877	-0.966091	-2.722031
H2B	4.385085	-1.15839	-1.915792
H3A	4.860749	-0.160593	0.420968
H3B	4.349119	1.493782	0.759407
H4B	2.387238	0.616873	2.073906
H4A	3.969898	0.196851	2.752864

H5B	1.726316	-2.257901	3.225359
H5A	1.008726	-0.907781	2.325541
H6A	0.085813	-3.034404	1.514102
H6B	1.69746	-3.691344	1.213548
H7	1.913228	3.018478	-0.612579
H8	1.198392	5.356482	-0.20719
H9	-1.194516	5.79153	0.423617
H10	-2.756824	3.867917	0.604497
H18	-5.878014	-0.981666	0.434325
H17	-5.613968	-3.393363	-0.070868
H16	-3.388659	-4.306838	-0.675508
H15	-1.417579	-2.853215	-0.764569

***endo*-4b**

E(RB3LYP)	-2187.55117590 A.U.
Zero-point correction	0.352469 (Hartree/Particle)
Thermal correction to Energy	0.375801
Thermal correction to Enthalpy	0.376745
Thermal correction to Gibbs Free Energy	0.299359
Sum of electronic and zero-point Energies	-2187.198707
Sum of electronic and thermal Energies	-2187.175375
Sum of electronic and thermal Enthalpies	-2187.174431
Sum of electronic and thermal Free Energies	-2187.251817

Atom Label	**X coord**	**Y coord**	**Z coord**
Pd1	0.560518	0.192325	-0.366873
S1	1.121304	-2.072196	-0.836919
S2	3.01536	0.65681	-0.586033
O1	2.006547	-0.805335	2.043441
S3	-3.825666	1.050016	0.287878
N1	-0.01119	2.224494	-0.169002
C1	2.611049	-1.801837	-1.891111
C2	3.690147	-0.908944	-1.298212
C3	3.689981	0.659337	1.134867
C4	3.408743	-0.578041	1.97415
C5	1.5759	-2.158005	2.005643
C6	1.826479	-2.882301	0.680501
C7	0.792459	3.294594	-0.231169
C8	0.318968	4.591236	-0.079937
C9	-1.043495	4.781511	0.14017
C10	-1.883874	3.677925	0.194101
C11	-1.346659	2.397545	0.032218
C12	-2.083352	1.155897	0.038767
C13	-1.461854	-0.05207	-0.162471
C14	-2.409905	-1.145324	-0.118776

C19	-3.738747	-0.691847	0.121446
C18	-4.824772	-1.565744	0.212585
C17	-4.595825	-2.926109	0.060576
C16	-3.297569	-3.404677	-0.181698
C15	-2.22258	-2.534524	-0.270999
H1A	3.019328	-2.785296	-2.131744
H1B	2.197685	-1.375414	-2.805648
H2A	4.393462	-0.626517	-2.082024
H2B	4.254167	-1.415068	-0.517731
H3A	4.765062	0.831573	1.064059
H3B	3.233372	1.541729	1.585599
H4B	3.805754	-0.397753	2.980574
H4A	3.936235	-1.449128	1.57749
H5B	2.061888	-2.747177	2.794075
H5A	0.507697	-2.125928	2.220902
H6A	1.358493	-3.866279	0.728274
H6B	2.886451	-3.037539	0.484893
H7	1.841899	3.107688	-0.414529
H8	1.008046	5.423021	-0.136625
H9	-1.447214	5.779053	0.263651
H10	-2.946908	3.800497	0.35622
H18	-5.823924	-1.189563	0.398561
H17	-5.425054	-3.620618	0.128036
H16	-3.133942	-4.469308	-0.302217
H15	-1.238173	-2.930365	-0.471759

Transition state – 4b

Atom Label	**X coord**	**Y coord**	**Z coord**
Pd1	0.555619	0.143828	-0.406842
S1	1.002192	-2.179503	-0.792482
S2	3.06348	0.542786	-0.614238
O1	2.300327	-1.05791	1.46656
S3	-3.755346	1.20017	0.402396
N1	0.081099	2.200423	-0.242307
C1	2.632586	-2.04031	-1.649395
C2	3.692792	-1.1511	-1.020018
C3	3.694767	0.805178	1.106043
C4	3.192345	-0.218659	2.159778
C5	1.712915	-2.219464	2.000811
C6	1.384001	-3.095381	0.782593
C7	0.922509	3.234678	-0.375334
C8	0.514051	4.552335	-0.21712
C9	-0.821732	4.803841	0.089004
C10	-1.702517	3.738196	0.212829
C11	-1.231364	2.433942	0.035727
C12	-2.021548	1.226942	0.083276

C13	-1.468883	-0.005309	-0.168636
C14	-2.471428	-1.049018	-0.128089
C19	-3.764094	-0.537831	0.182768
C18	-4.889945	-1.358203	0.287363
C17	-4.740239	-2.720588	0.069059
C16	-3.481849	-3.253324	-0.256472
C15	-2.366772	-2.436366	-0.355834
H1A	3.016748	-3.056406	-1.762987
H1B	2.350814	-1.680244	-2.640362
H2A	4.510902	-1.026913	-1.73149
H2B	4.085973	-1.583004	-0.105001
H3A	4.78207	0.809061	1.036804
H3B	3.37474	1.818637	1.347383
H4B	2.69419	0.300219	2.986299
H4A	4.032806	-0.792971	2.56539
H5B	2.401673	-2.761891	2.65903
H5A	0.809719	-1.969669	2.568301
H6A	0.512617	-3.72327	0.966916
H6B	2.220808	-3.742949	0.519212
H7	1.948535	3.001094	-0.625307
H8	1.231822	5.352916	-0.334536
H9	-1.17424	5.819372	0.222323
H10	-2.747448	3.908207	0.437696
H18	-5.859297	-0.938995	0.530506
H17	-5.601606	-3.37394	0.144352
H16	-3.381916	-4.317417	-0.436507
H15	-1.416481	-2.870199	-0.630541

[Pd(btp)(9[ane]S3)]$^{+}$

E(RB3LYP)	-2510.53296925 A.U.
Zero-point correction	0.348753 (Hartree/Particle)
Thermal correction to Energy	0.372741
Thermal correction to Enthalpy	0.373685
Thermal correction to Gibbs Free Energy	0.294856
Sum of electronic and zero-point Energies	-2510.184216
Sum of electronic and thermal Energies	-2510.160228
Sum of electronic and thermal Enthalpies	-2510.159284
Sum of electronic and thermal Free Energies	-2510.238113

Atom Label	**X coord**	**Y coord**	**Z coord**
Pd1	0.504918	0.244866	-0.367999
S1	1.06239	-1.952701	-1.10131
S2	2.915136	0.787862	-0.720319
S3	1.78712	-0.794237	2.267976
S4	-3.915876	0.987673	0.201208
N1	-0.120391	2.264931	-0.122929

C1	2.49178	-1.556714	-2.20041
C2	3.584659	-0.712823	-1.565107
C3	3.750738	0.750758	0.924762
C4	3.543254	-0.467062	1.823906
C5	1.512857	-2.520144	1.702001
C6	1.892376	-2.89178	0.271968
C7	0.6582	3.355079	-0.130097
C8	0.145933	4.6379	0.010067
C9	-1.230888	4.793011	0.159281
C10	-2.044646	3.668709	0.162647
C11	-1.467679	2.403274	0.017189
C12	-2.171101	1.143201	-0.0045
C13	-1.509491	-0.048805	-0.169001
C14	-2.42223	-1.170792	-0.114088
C15	-3.770612	-0.754053	0.07783
C16	-4.830291	-1.659982	0.165332
C17	-4.553413	-3.016392	0.06694
C18	-3.233169	-3.460018	-0.115282
C19	-2.185271	-2.557533	-0.204307
H1	2.900536	-2.504725	-2.55541
H2	2.032537	-1.048172	-3.048218
H3	4.270735	-0.367868	-2.339215
H4	4.16556	-1.276601	-0.838149
H5	4.816984	0.887186	0.732302
H6	3.387459	1.658055	1.409955
H7	4.084864	-0.275917	2.752319
H8	3.976449	-1.368954	1.393443
H9	2.062015	-3.195665	2.36151
H10	0.449537	-2.682499	1.885282
H11	1.62057	-3.935105	0.103966
H12	2.965299	-2.810455	0.111515
H13	1.720099	3.196026	-0.259909
H14	0.816112	5.486809	-0.001985
H15	-1.665042	5.779328	0.268932
H16	-3.117222	3.76298	0.272971
H17	-5.845983	-1.311232	0.31047
H18	-5.361596	-3.735343	0.133383
H19	-3.030662	-4.522268	-0.187597
H20	-1.182767	-2.929674	-0.354754