Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information (ESI)

New 7-Azaindole Palladium and Platinum Complexes: Crystal Structures and Theoretical Calculations. *In Vitro* Anticancer Activity of the Platinum Compounds

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Table of contents

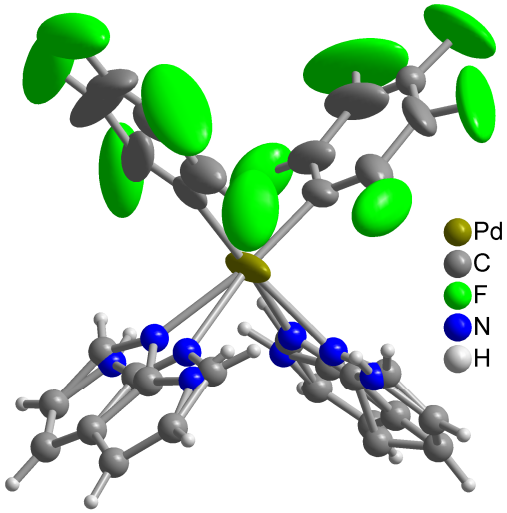


Figure SI 1. Molecular structure of **1** with the azaindole atoms in ball-and-stick representation, Pd and the C_6F_5 groups as ellipsoids (50%). The disorder of the azaindole ligand and the high temperature factors with the ellipsoid shape of the C_6F_5 group atoms are explained bellow and with Fig. 1 and SI 2. Part of the disordered atoms have been removed for clarity, the para-C atoms of the right C_6F_5 group was non-positive defined.

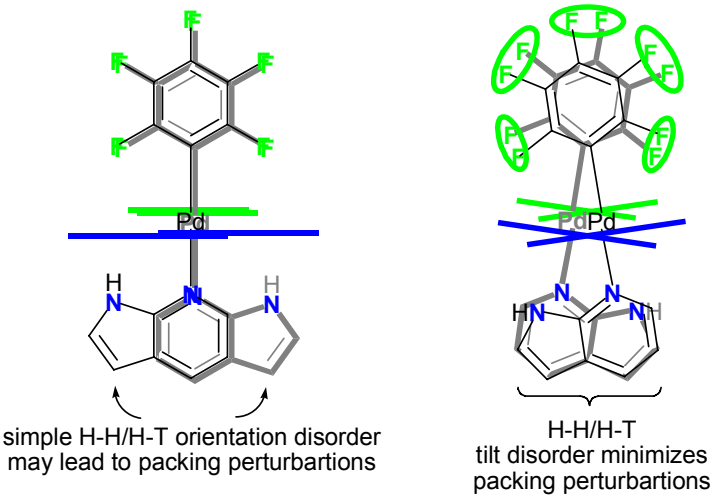


Figure SI 2. Schematic explanation of the observed H-H/H-T tilt disorder (right) which minimizes packing perturbations versus a simple orientation disorder (left). A consequence of the tilt disorder at the right are high temperature factors of the C_6F_5 group atoms which are akin to a (not possible) rotational movement around the pseudo C_6 axis of the ring. The effect of this tilt disorder on the respective cis-azaindole and -C_6F_5 group (here perpendicular to the projection plane, represented as blue and green bars) is in additional out-of-plane tilt disorder.

In the absence of any stronger H-bonding interactions which would help to stabilize one orientation over the other (cf. compound **3** and **4**) both dispositions are about equally occupied. Indeed quantum chemical calculations performed on the platinum complex **2** revealed that the C_2-symmetric H-T isomer is more stable. Its optimized geometry features two identical *ortho*-F···HN hydrogen bonds ($d_{H\cdots F}$ = 2.044 Å) that considerably turns the Haza ligand (dihedral C–Pt–N7–N1 68.8º) thus avoiding repulsive interactions between both heterocycles. In the diffraction analysis, two half-occupied positions were refined for the clearly disordered pyrrole and pyridine N atoms and the C atoms of the central C–C bond between the rings. This disorder is accompanied by different tilt orientations of the two C–Pd–N axes of the molecule in its available space in order to minimize packing perturbations (Fig. SI 2). This tilt disorder occurs for both azaindole rings (Fig. SI 1) and affects the respective other cis-azaindole and -C_6F_5 group therefore inducing there also a slight out-of-plane tilt disorder so as to retain the square-planar coordination at the Pd atom (Fig. SI 1). Hence, the H-H/H-T disorders of both azaindole rings affect each other as well as the C_6F_5 groups and lead to at least four different tilt orientations for each molecule. Thus, the structure of **1** with its inherent disorder and also because of the problematic needle-shape of the crystals could not be refined to satisfactory *R*-values and statistics.

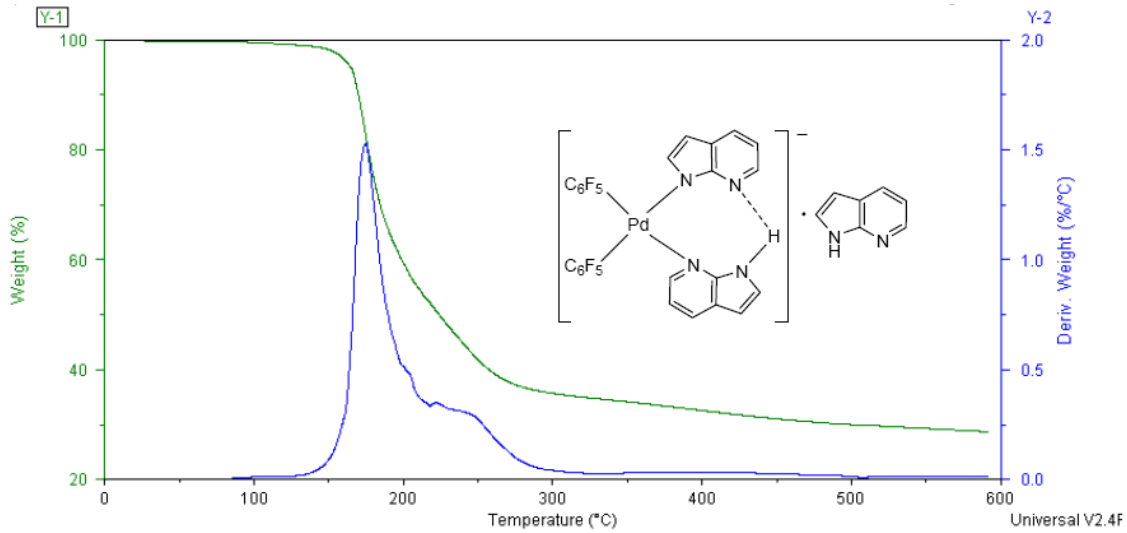


Figure SI 3. TGA-DTA of complex **3**.

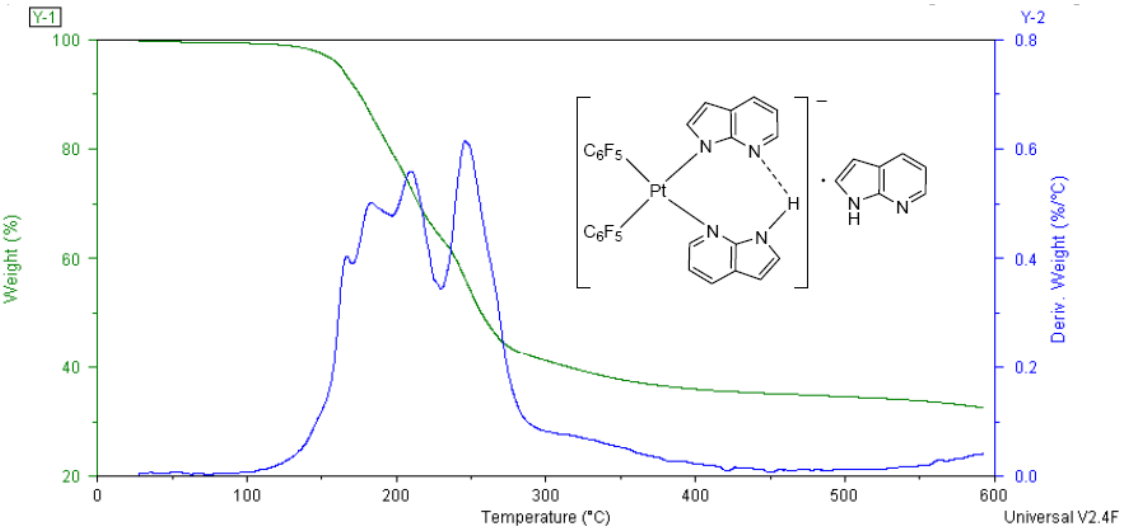


Figure SI 4. TGA-DTA of complex **4**.

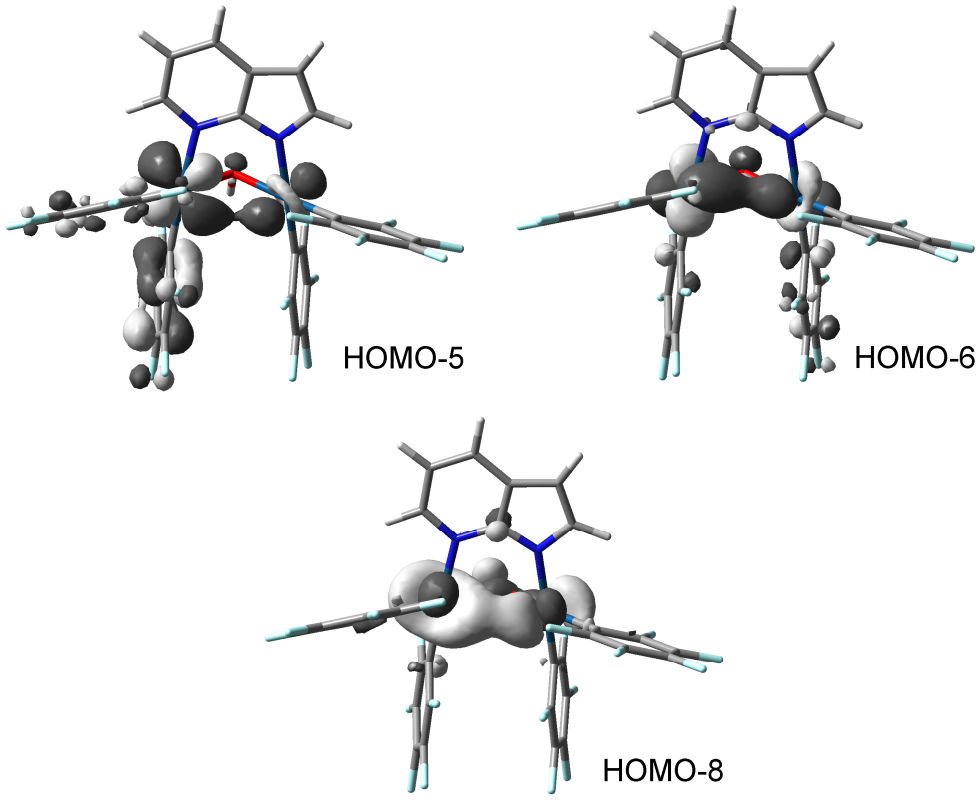


Figure SI 5. Calculated HOMO-5, HOMO-6 and HOMO-8 (0.04 isovalue) surfaces for complex $\mathbf{6}^{calc}$.

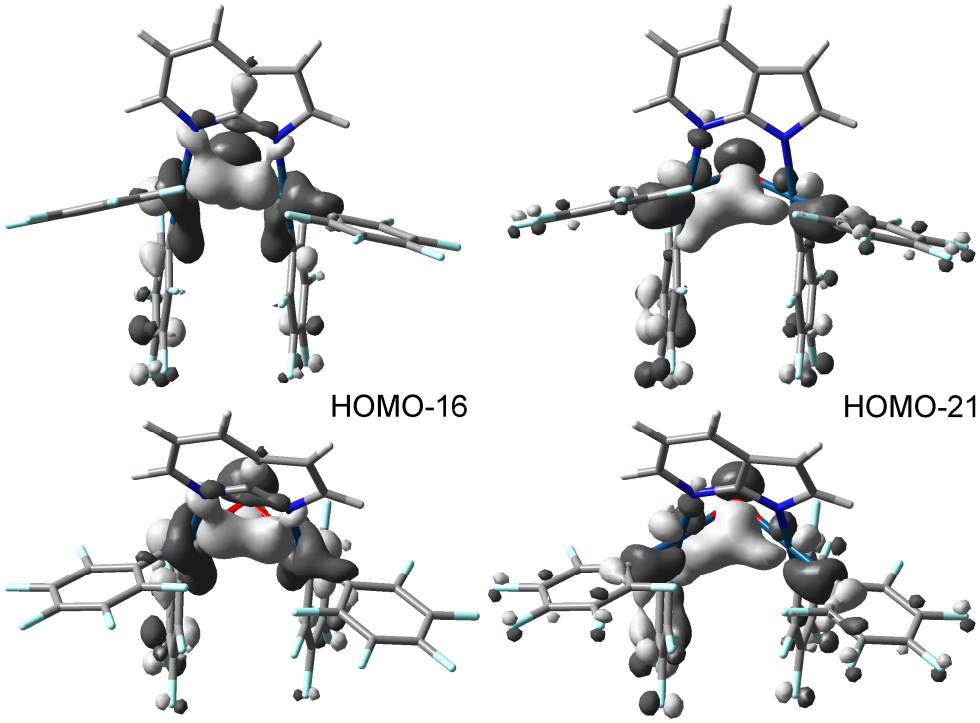


Figure SI 6. Calculated HOMO-16, and HOMO-21 (0.04 isovalue) surfaces for complex $\mathbf{6}^{calc}$ in front (up) and tilted (down) views.

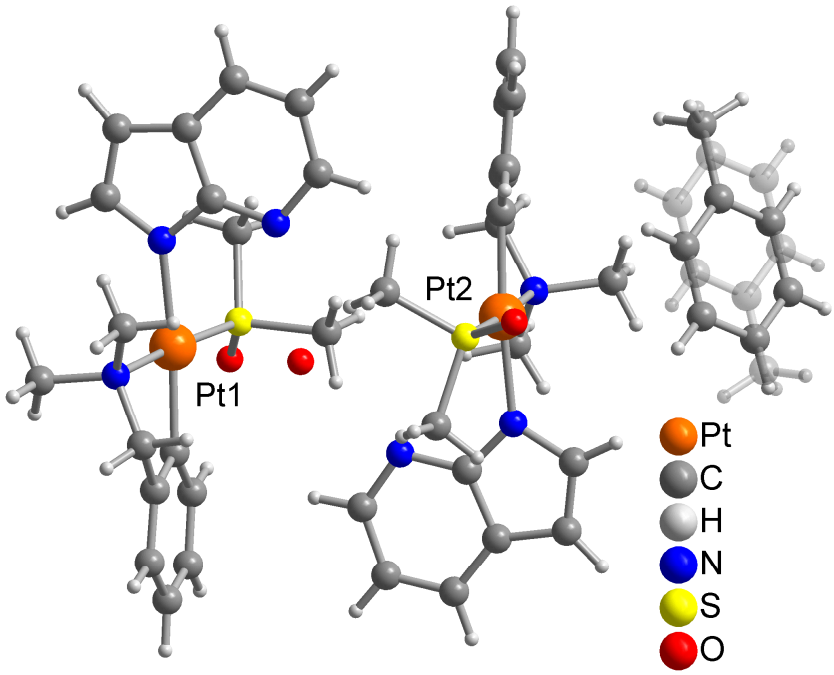
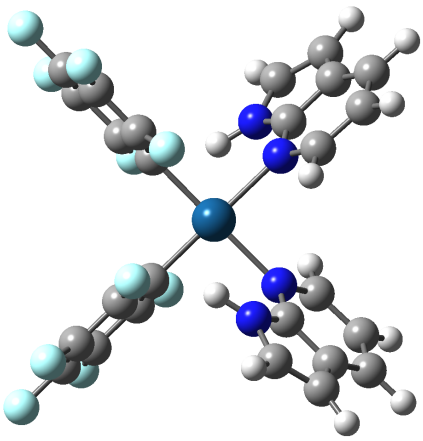


Figure SI 7. Structure of **9**·0.5H_2O·0.25C_7H_8 illustrating the toluene disorder around the inversion center. Each of the symmetry-related toluene molecules (differentiated by normal and transparent representation) are half-occupied.

Calculated structures.- Cartesian coordinates (Å) and energies (au) for **2**, $\mathbf{2}^{\cdot+}$ and **3**.-



Complex $\mathbf{2}^{\mathbf{HT}}$ (C_2): E = - 2334.46507853 au

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C	2.01580211	0.00000000	0.00000000	C	-4.96097816	-0.46458853	0.08675918
C	2.80045146	1.15404123	0.00000000	C	-4.13136262	-1.34065427	0.80695146
C	4.19887845	1.14294827	0.00383994	C	-4.30156851	-2.47861368	1.66057476
C	4.86312967	-0.08901992	0.01724053	C	-3.03969463	-2.87623631	2.05406913
C	4.11972708	-1.27615262	0.00633183	H	-2.46746518	1.50645941	-1.21227881
C	2.72235742	-1.20787254	-0.00281244	H	-4.95746421	1.27171214	-1.21172915
F	2.19047218	2.38827670	-0.04661772	H	-6.04719574	-0.57778399	0.09772091
F	4.90699831	2.29025154	-0.00955571	H	-5.23787567	-2.94593699	1.95147878
F	6.20866344	-0.13271058	0.02310351	H	-2.73395923	-3.69053911	2.70512317
F	4.75950678	-2.46253147	0.00249897	H	-1.07104707	-2.06515783	1.65226635
F	2.04140979	-2.38935496	-0.03555745	N	0.86711792	1.72259520	-2.64982648
C	-0.00448604	0.55043889	1.93918956	C	0.40311453	0.47303171	-2.96254545
C	-0.33858644	1.86024087	2.30109941	N	-0.00762573	-0.46293871	-2.08279242
C	-0.35154279	2.30739399	3.62672106	C	-0.42978943	-1.63467180	-2.61144968
C	-0.01854300	1.41484078	4.65361530	C	-0.45448162	-1.87920883	-3.99473617
C	0.30644674	0.09002719	4.33992022	C	-0.03235662	-0.90193560	-4.90103460
C	0.30889234	-0.30310470	2.99784098	C	0.41939493	0.32480291	-4.38580502
F	-0.69118810	2.75887162	1.33735785	C	0.93021734	1.55598235	-4.91102061
F	-0.68060689	3.57880594	3.93012735	C	1.19737233	2.37205404	-3.83031660
F	-0.02782664	1.82422360	5.93608357	H	-0.74935216	-2.38680987	-1.88919011
F	0.60526845	-0.78170629	5.32414885	H	-0.80738128	-2.84938032	-4.34639645
F	0.60242582	-1.62394232	2.73936192	H	-0.05030287	-1.09091520	-5.97656518
N	-2.08067674	-2.05470480	1.47979385	H	1.08454039	1.80930216	-5.95586702
C	-2.72168366	-1.10755164	0.72712364	H	1.60064489	3.38039405	-3.79778467
N	-2.13002777	-0.12207373	0.02179446	H	1.02793513	2.05336314	-1.69382535
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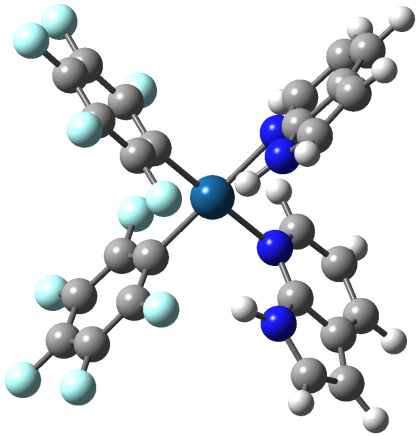

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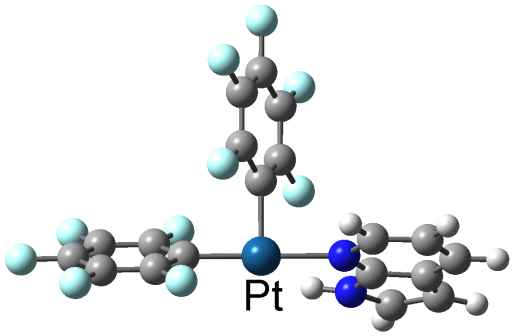
C	2.71537660	1.21461981	0.00000000	C	-4.28736738	-1.15452676	0.19603239
C	4.11191917	1.29913773	-0.01329132	C	-4.60747581	-2.51767877	0.49985298
C	4.86937320	0.12132452	-0.03126580	C	-3.41018018	-3.17423196	0.69862799
C	4.21692355	-1.11601039	-0.04810167	H	-2.27069866	2.08644087	-0.39583718
C	2.81850943	-1.14329758	-0.02807932	H	-4.76403274	2.14104981	-0.50006344
F	2.02333384	2.38741030	0.00194562	H	-6.08712737	0.03573708	-0.11829298
F	4.73690095	2.49305644	-0.01186681	H	-5.59757339	-2.95883115	0.56864787
F	6.21413625	0.17957468	-0.04786262	H	-3.21609584	-4.21062263	0.96067222
F	4.93477638	-2.25694354	-0.08755689	H	-1.36141699	-2.47370794	0.71183772
F	2.23564167	-2.39266075	-0.07461037	N	0.79917399	-1.95715398	-2.56950965
C	-0.03180353	-0.22249735	2.00568330	C	0.38036791	-0.71179808	-2.95001399
C	-0.17673647	0.90073273	2.82948867	N	0.01910309	0.28944452	-2.12252358
C	-0.22126831	0.82885039	4.22609263	C	-0.33396439	1.45218186	-2.71862250
C	-0.12117560	-0.42030670	4.85130481	C	-0.36049268	1.61839102	-4.11326575
C	0.00882435	-1.57272254	4.06899512	C	-0.00595250	0.56741983	-4.96405082
C	0.05376513	-1.44336196	2.67689102	C	0.38959428	-0.64687463	-4.37980295
F	-0.29323710	2.13598707	2.26829395	C	0.84680987	-1.92566294	-4.83654499
F	-0.36136586	1.93973524	4.97599507	C	1.09785959	-2.68493391	-3.71201353
F	-0.16527986	-0.51279120	6.19352580	H	-0.58755775	2.26914987	-2.04247127
F	0.08412446	-2.78339373	4.65823455	H	-0.65788983	2.58677065	-4.51729157
F	0.15447956	-2.61853583	1.96160889	H	-0.02562120	0.69369018	-6.04867915
N	-2.35032203	-2.29899393	0.51194145	H	0.97939189	-2.24495521	-5.86616367
C	-2.85917036	-1.06342308	0.21948471	H	1.46944684	-3.70206722	-3.62367216
N	-2.14153225	0.05492167	-0.00863622	H	1.00151925	-2.21724947	-1.60006477
C	-2.85656139	1.17835970	-0.25064992				



Complex **7**: E = -1954.63754842 au

E^{+1e} = -1954.68552614 au

E^{-1e} = -1954.37411605 au

Pt	0.00000000	0.00000000	0.00000000		F	0.92808900	-0.00773241	5.24359134
C	1.99523499	0.00000000	0.00000000		F	-0.03805838	-2.55378391	5.58105438
C	2.71250224	1.20577024	0.00000000		F	-0.98079440	-3.95804557	3.41696869
C	4.10931475	1.25708510	-0.01370574		F	-0.95755561	-2.84312888	0.94354449
C	4.83266879	0.05718860	-0.01693962		N	-2.28936453	-1.90127005	-1.48771423
C	4.15642497	-1.16991940	-0.00856368		C	-2.83038965	-0.90584008	-0.72145147
C	2.75828088	-1.17655201	0.00262479		N	-2.13787232	-0.00000242	-0.00000475
F	2.04082581	2.38710394	0.00238940		C	-2.87954672	0.90035389	0.69192234
F	4.76661561	2.43256260	-0.02652413		C	-4.28290847	0.91320742	0.65850333
F	6.17643189	0.08278832	-0.03622056		C	-4.99008733	-0.02397172	-0.10174631
F	4.86027429	-2.31862549	-0.01641267		C	-4.25453684	-0.98079740	-0.82004455
F	2.14123240	-2.38749302	0.02000928		C	-4.53916751	-2.09442435	-1.67687178
C	-0.00000133	-0.81792950	1.78703271		C	-3.32617944	-2.63621320	-2.04746455
C	0.47944629	-0.12435334	2.90515305		H	-2.31057072	1.62223567	1.27892377
C	0.47103613	-0.69817963	4.18340340		H	-4.81055077	1.67107104	1.23851518
C	-0.02202823	-1.99636284	4.35811604		H	-6.08178516	-0.01328449	-0.12807652
C	-0.50588140	-2.70941251	3.25489570		H	-5.51777202	-2.45226658	-1.98319248
C	-0.48404468	-2.11486048	1.98882552		H	-3.10613653	-3.49323253	-2.67763313
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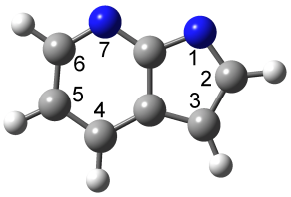
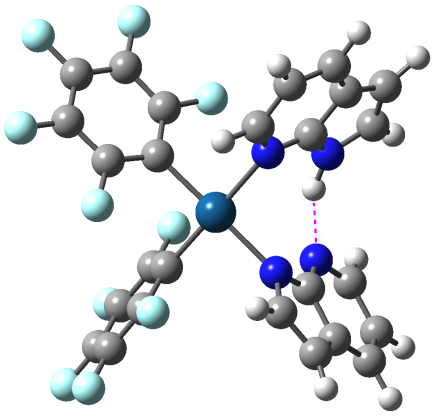


7-Azaindolate (*"aza"*): E = -379.189627464 au

E^{+1e} = -378.968302693 au

E^{-1e} = -379.097614410 au

C	0.00000000	0.00000000	0.00000000		C	2.83729993	3.52440010	0.00000000
C	1.40493620	0.00000000	0.00000000		C	2.94711499	2.12938529	0.00000000
C	1.76325467	1.37302775	0.00000000		H	1.47687041	5.21955745	0.00000000
C	0.48748279	2.09847247	0.00000000		H	3.72924179	4.15973401	0.00000000
N	-0.58037412	1.24158914	0.00000000		H	3.93289120	1.64671467	0.00000000
N	0.38973961	3.45279584	0.00000000		H	2.06889127	-0.86609165	0.00000000
C	1.55651608	4.12324717	0.00000000		H	-0.64262204	-0.88758146	-0.00000000



Complex **8**: E = -2333.93962268 au

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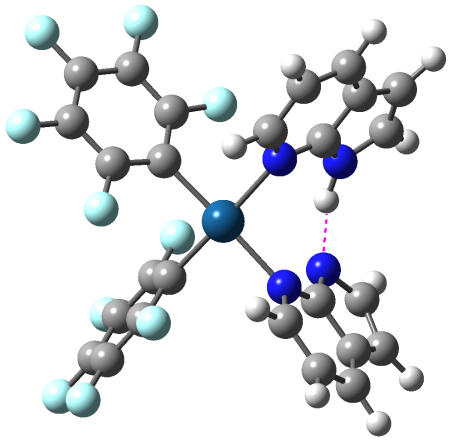
C	2.75476478	1.19313419	0.00000000		C	2.79120259	-1.16907682	-0.01246168
C	4.15303483	1.24281919	-0.01113589		F	2.10510269	2.39587349	0.00577680

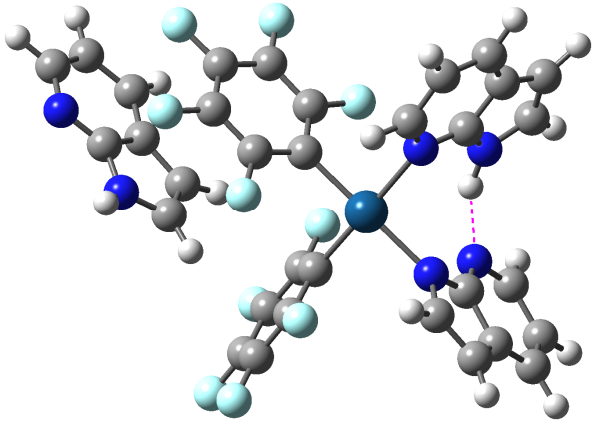
F	4.81777216	2.42451424	-0.00774257	C	-4.24688438	-0.90623632	0.07249244
F	6.23250494	0.06833291	-0.02791267	C	-2.93057045	-1.05674684	-0.35746459
F	4.89375298	-2.33128405	-0.04414255	H	-3.14237831	3.65090334	2.38968597
F	2.18343549	-2.38931685	-0.03528394	H	-5.51081728	2.90568531	2.64231842
C	-0.01871685	-1.02580114	1.72412784	H	-6.26803435	0.75455321	1.57913881
C	0.27853442	-0.41783044	2.94812364	H	-5.07174962	-1.59126764	-0.11324786
C	0.23692362	-1.10029667	4.16978255	H	-2.49322758	-1.87804551	-0.92190976
C	-0.11148478	-2.45460412	4.18546176	N	-0.95326159	3.09014150	-0.80017469
C	-0.41106134	-3.10252078	2.98276301	C	-0.38074295	2.41276031	-1.83803492
C	-0.35688447	-2.38104794	1.78514998	N	0.05259452	1.13543419	-1.80929890
F	0.63026888	0.89770147	2.98944883	C	0.61098669	0.66984453	-2.94906529
F	0.52798634	-0.47375654	5.33643081	C	0.74467269	1.44885291	-4.11184024
F	-0.15714391	-3.13439576	5.35690929	C	0.30161962	2.77431357	-4.13533986
F	-0.74418482	-4.41702775	2.99875923	C	-0.28513566	3.29182708	-2.96914294
F	-0.65114861	-3.06429281	0.64295116	C	-0.85103304	4.53796942	-2.55151965
N	-2.12040683	-0.01131045	0.03540215	C	-1.25023728	4.36493040	-1.23820348
C	-2.92641635	0.83666555	0.74682721	H	0.96785565	-0.35989218	-2.90036054
N	-2.52356100	2.00560237	1.28909494	H	1.20971018	0.99925078	-4.99090395
C	-3.46924150	2.70242298	1.94946227	H	0.41255282	3.38771518	-5.03335841
C	-4.80808038	2.28131968	2.08522825	H	-0.94894303	5.44619347	-3.14034849
C	-5.22701112	1.08295098	1.49588615	H	-1.73582485	5.06311581	-0.56103052
C	-4.27820764	0.31782077	0.79984064	H	-1.28177846	2.66917297	0.10785869



Complex **8**$^{\mathbf{isom}}$: E = -2333.93629870 au

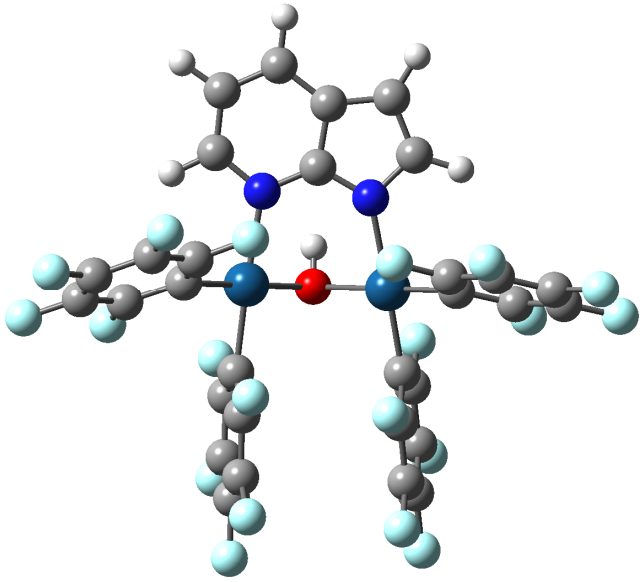
Pt	0.00000000	0.00000000	0.00000000	C	-2.81138800	-1.04014284	-0.63656256
C	2.01053023	0.00000000	0.00000000	N	-2.13570255	-0.08471503	0.03894065
C	2.77199191	1.17229692	0.00000000	C	-2.87214953	0.71567861	0.84339983
C	4.17097839	1.17743811	-0.03401700	C	-4.26343587	0.58331060	0.99197808
C	4.85812024	-0.04008671	-0.06128021	C	-4.95978920	-0.41469045	0.30378680
C	4.13638609	-1.23809768	-0.05274881	C	-4.22918698	-1.26222534	-0.54351949
C	2.73755392	-1.19566187	-0.01863358	C	-4.51041833	-2.37011423	-1.40272298
F	2.15749638	2.38959963	0.03780725	C	-3.29897702	-2.74794253	-1.95636550
F	4.87049614	2.33913624	-0.03550422	H	-2.30319415	1.46923876	1.38981377
F	6.21235618	-0.05884875	-0.09400669	H	-4.78436266	1.26731529	1.66426101
F	4.80388889	-2.41731227	-0.07489105	H	-6.03996083	-0.53109817	0.42627775
F	2.08698789	-2.39024347	0.00285578	H	-5.47752696	-2.83034428	-1.58793616
C	0.00047823	-0.55808521	1.93864888	H	-3.08059912	-3.53735029	-2.67177616
C	0.56373518	0.21897020	2.95855866	H	-1.27336959	-1.93657499	-1.89879324
C	0.55282361	-0.15426107	4.30813966	N	0.02041053	-1.60699188	-2.94022377
C	-0.04374854	-1.36309439	4.67920649	C	0.15076886	-0.26075798	-3.06875250
C	-0.62478145	-2.17159585	3.69713518	N	0.05094818	0.63076503	-2.04555645
C	-0.58771856	-1.75747012	2.36112397	C	0.15343609	1.94569738	-2.35244388
F	1.14603624	1.41610596	2.66594807	C	0.38116945	2.41014867	-3.65847122
F	1.10255063	0.63763848	5.26134497	C	0.51873622	1.50728195	-4.72014282
F	-0.06768165	-1.74277840	5.97910337	C	0.39620473	0.13831629	-4.44435427
F	-1.20472750	-3.34270327	4.05601499	C	0.42400261	-1.08460212	-5.17296158
F	-1.17206044	-2.59078143	1.45194410	C	0.18522639	-2.08175638	-4.22501677
N	-2.26933786	-1.96042585	-1.48503260	H	0.07611036	2.62997953	-1.50730158

H	0.46144186	3.48660472	-3.82293641	H	0.59428089	-1.21636337	-6.24014710
H	0.70979738	1.86816853	-5.73579968	H	0.12159451	-3.15697635	-4.40587615



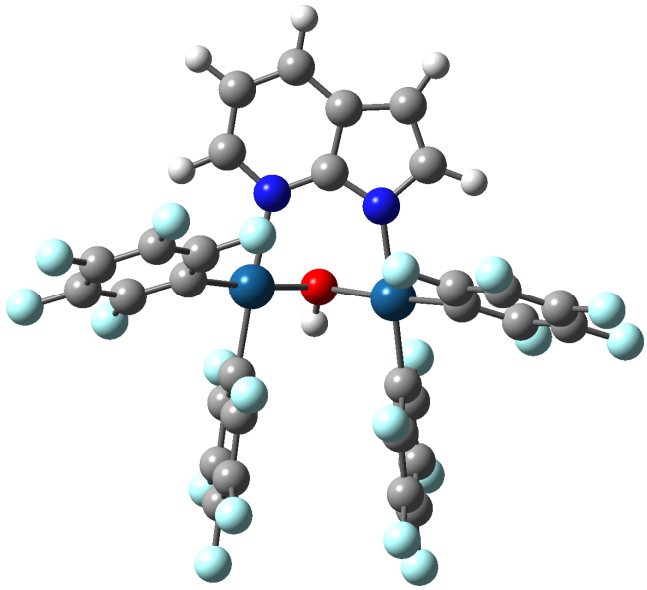
Complex **4**^{calc}: E = -2713.71966338 au

Pt	0.00000000	0.00000000	0.00000000	H	-6.27434785	1.07602785	1.35058604
C	2.02237195	0.00000000	0.00000000	H	-5.09888761	-1.51241175	0.04014842
C	2.73346083	1.20643768	0.00000000	H	-2.51400612	-1.95904031	-0.67203501
C	4.12977647	1.28444509	-0.00010292	N	-0.88034516	2.95046006	-1.25676902
C	4.87705795	0.10225147	-0.03195081	C	-0.31227986	2.11538579	-2.17554532
C	4.21202359	-1.12534699	-0.06349526	N	0.08368348	0.84411034	-1.95664905
C	2.81332129	-1.15150424	-0.02634067	C	0.63713552	0.20110882	-3.00963576
F	2.05582098	2.39279920	-0.00054219	C	0.80421562	0.79880965	-4.27094693
F	4.77126244	2.47705178	0.03478089	C	0.40304502	2.11937775	-4.49153615
F	6.22839168	0.14578201	0.01007969	C	-0.17840719	2.81774946	-3.42076808
F	4.93418299	-2.27729204	-0.05875370	C	-0.71309305	4.12591738	-3.19699918
F	2.23444035	-2.39106774	0.00741207	C	-1.13425650	4.15588887	-1.87944737
C	-0.03430299	-0.71465713	1.87285294	H	0.96259622	-0.82037070	-2.80810537
C	0.28241998	0.09414938	2.97001318	H	1.26237954	0.21298197	-5.06961371
C	0.23566658	-0.35187471	4.29571143	H	0.54084819	2.59253863	-5.46723304
C	-0.15693154	-1.66769337	4.56318815	H	-0.77742611	4.94141262	-3.91245818
C	-0.48524260	-2.51330629	3.49674807	H	-1.60707287	4.95810401	-1.31851785
C	-0.41999210	-2.02294016	2.18577514	H	-1.22874033	2.67454206	-0.30230465
F	0.69969243	1.37881029	2.78106883	N	4.47562330	-2.24580323	2.96016991
F	0.59033731	0.46550919	5.31629342	C	3.33988456	-1.48200938	3.18181673
F	-0.21157824	-2.12193014	5.83664506	C	3.69672536	-0.17612130	3.45310471
F	-0.87075456	-3.78722063	3.75151365	C	5.12597370	-0.11338053	3.36874717
F	-0.74957990	-2.89488372	1.19175140	C	6.11773011	0.87398964	3.49691031
N	-2.11889570	0.01915045	0.01460641	C	7.44643782	0.49318484	3.29361660
C	-2.91890154	0.97679373	0.57855479	C	7.76047248	-0.84239950	2.96551560
N	-2.50137722	2.20577633	0.94998207	N	6.84929062	-1.82429848	2.82668261
C	-3.44357805	3.00822757	1.48322292	C	5.58706424	-1.43078685	3.03570551
C	-4.79231409	2.63473693	1.65467133	H	4.49459233	-3.19530912	2.60129614
C	-5.22576373	1.37019915	1.23976241	H	2.35313522	-1.93029680	3.10174969
C	-4.28135036	0.49480342	0.68101634	H	3.00457916	0.63320774	3.66849840
C	-4.26311248	-0.82283355	0.14044548	H	5.85666184	1.90766835	3.73762059
C	-2.94349519	-1.05785075	-0.23812383	H	8.25287576	1.22525458	3.37590604
H	-3.10519648	4.00555317	1.78492489	H	8.80215491	-1.13415381	2.79638164
H	-5.49118051	3.34638446	2.10083414				



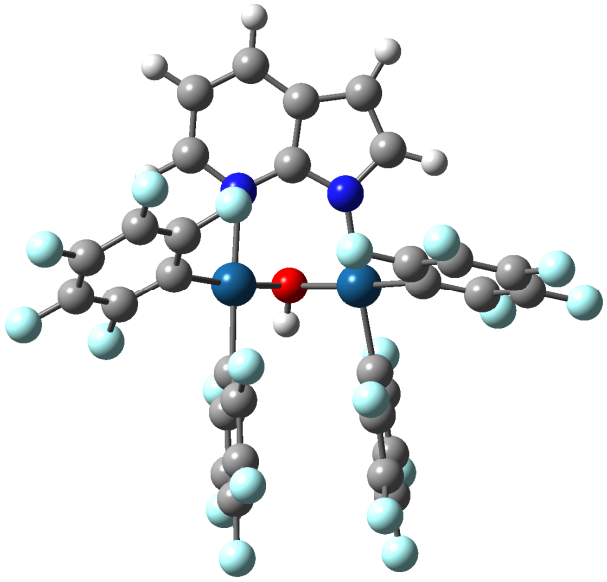
Complex **6**$^{\mathbf{diast}}$: E = -3604.90509848 au

Pt	0.00000000	0.00000000	0.00000000	F	3.76716749	3.74549596	3.25281828
C	2.00491723	0.00000000	0.00000000	F	5.33575780	1.72057585	4.25308767
C	2.78462337	1.16253383	0.00000000	F	4.21893802	-0.72580065	4.81503738
C	4.18147640	1.15496478	0.09414691	F	1.57598414	-1.15675540	4.38835010
C	4.85544794	-0.06647742	0.17664912	C	-1.35406336	2.17678806	4.12216607
C	4.11939818	-1.25526635	0.16931115	C	-2.18894786	3.16105828	3.56480839
C	2.72442964	-1.20025749	0.08004658	C	-2.72960505	4.22285480	4.29870645
F	2.19168277	2.38661317	-0.07846344	C	-2.43371993	4.33918318	5.66035774
F	4.89312848	2.31229931	0.11648195	C	-1.61106298	3.38400593	6.26339118
F	6.21171151	-0.10033250	0.26156913	C	-1.09343944	2.33657175	5.49179050
F	4.77853713	-2.44454431	0.23191422	F	-2.51136544	3.11526552	2.24508436
F	2.07398213	-2.39829119	0.05337890	F	-3.52633944	5.15527474	3.71304099
C	-0.08696834	0.96380369	-1.74523890	F	-2.95036978	5.36259030	6.39230446
C	-0.81613589	2.15737456	-1.89005419	F	-1.34086171	3.48324573	7.59395390
C	-0.93816658	2.84501810	-3.10315101	F	-0.31859397	1.43162745	6.15803447
C	-0.30931727	2.34284648	-4.24677975	O	0.08873561	-1.01241811	1.89646803
C	0.42416300	1.15702238	-4.15597124	H	-0.62679716	-1.67611151	1.86453992
C	0.51972844	0.50092795	-2.92286009	N	-2.12230362	-0.16569281	0.07244358
F	-1.45102639	2.70323136	-0.82098387	C	-2.97125289	-0.14904893	1.14060096
F	-1.64868517	4.00062647	-3.19351234	N	-2.64311503	0.12745956	2.43126852
F	-0.41708732	2.99621917	-5.43546117	C	-3.64336389	0.08599970	3.34293691
F	1.02003861	0.65533514	-5.27311860	C	-4.97650291	-0.21587017	3.01787493
F	1.23279808	-0.66352160	-2.92018759	C	-5.33276048	-0.49274360	1.69441813
Pt	-0.65963415	0.64870860	3.03781716	C	-4.32566671	-0.46745789	0.71908862
C	1.24020887	1.05706984	3.53055729	C	-4.24500315	-0.67683825	-0.68475333
C	1.85033412	2.29521560	3.29193582	C	-2.90617250	-0.48543095	-1.01573284
C	3.21228561	2.53374512	3.51288181	H	-3.34140980	0.31708503	4.36571878
C	4.01520056	1.50708019	4.01755410	H	-5.72227941	-0.22088010	3.81622936
C	3.44282504	0.26110240	4.29236083	H	-6.37012486	-0.72106373	1.42810748
C	2.07777720	0.06440830	4.05681321	H	-5.05708895	-0.92761481	-1.36471968
F	1.12497400	3.34151130	2.80985034	H	-2.42956699	-0.55511174	-1.99265215



Complex **6**^{calc}: E = -3604.90926610 au

Pt	0.00000000	0.00000000	0.00000000	F	3.65988575	3.75251680	3.49524937
C	2.00994680	0.00000000	0.00000000	F	5.31443253	1.75147613	4.39451378
C	2.78729646	1.16731940	0.00000000	F	4.31945642	-0.79149212	4.74102000
C	4.18687556	1.16426748	0.02875411	F	1.72022472	-1.33287450	4.19708009
C	4.87191110	-0.05405641	0.06553915	C	-1.32998203	1.96860061	4.20823159
C	4.14298216	-1.24645469	0.07429378	C	-2.18671485	2.96588909	3.70958094
C	2.74524794	-1.19317631	0.04288784	C	-2.72781299	3.98626660	4.49939582
F	2.18929966	2.38973947	-0.01923967	C	-2.40829544	4.04767138	5.85940235
F	4.89509421	2.32321526	0.03488212	C	-1.56195470	3.07852117	6.40471447
F	6.22999595	-0.07917737	0.09509458	C	-1.04556870	2.07318783	5.57843557
F	4.80673226	-2.43362168	0.10021284	F	-2.52961279	2.97576448	2.39458170
F	2.09592967	-2.39791836	0.04426211	F	-3.54602418	4.93330133	3.96935003
C	-0.07124129	1.06494034	-1.68640616	F	-2.92372629	5.03168373	6.64457584
C	-0.79345382	2.26902478	-1.76878726	F	-1.26794332	3.12248939	7.73334347
C	-0.89846863	3.02717803	-2.94067002	F	-0.24710645	1.14922465	6.19073752
C	-0.25708699	2.59180992	-4.10468059	O	-0.05162412	-1.14731268	1.80761666
C	0.47154122	1.39990572	-4.07525023	H	0.86013239	-1.40222014	2.04079517
C	0.54888556	0.67149838	-2.88229983	N	-2.11472744	-0.13912609	0.06006259
F	-1.43568327	2.75597764	-0.67628546	C	-2.94769924	-0.21149856	1.13686451
F	-1.60235082	4.19004737	-2.97024654	N	-2.61427746	-0.00603370	2.43794067
F	-0.34687885	3.31603518	-5.25328324	C	-3.60114026	-0.12376737	3.35569239
F	1.07932472	0.96212168	-5.21280636	C	-4.93137489	-0.43445139	3.02677932
F	1.25722248	-0.49541578	-2.94043769	C	-5.29603986	-0.63555585	1.69202967
Pt	-0.63581816	0.49842865	3.04513340	C	-4.30066744	-0.52938234	0.71054958
C	1.26625471	0.92812199	3.53275044	C	-4.23426572	-0.64497370	-0.70504420
C	1.82494774	2.20627302	3.37920201	C	-2.90383829	-0.40403072	-1.03770954
C	3.16458420	2.49970673	3.66045338	H	-3.29237336	0.05058682	4.38767554
C	4.01303793	1.48530996	4.11398205	H	-5.66768933	-0.50569871	3.83080186
C	3.50387503	0.19459199	4.28272187	H	-6.33160479	-0.86798963	1.42185867
C	2.15709711	-0.04920324	3.99447001	H	-5.04969947	-0.86822521	-1.39059261
F	1.06715543	3.24232301	2.93172644	H	-2.43778673	-0.40280680	-2.02222821



Complex **6** $^{+}$: E = -3604.88541950 au

Pt	0.00000000	0.00000000	0.00000000
C	2.02570811	0.00000000	0.00000000
C	2.82080868	1.15293783	0.00000000
C	4.21751290	1.11621304	0.07110533
C	4.87386719	-0.11869743	0.12316446
C	4.12210939	-1.29799819	0.10583047
C	2.72725899	-1.21209613	0.04500937
F	2.24962961	2.38510716	-0.03705601
F	4.93923805	2.25695708	0.12658517
F	6.22027193	-0.17099564	0.19110946
F	4.74993731	-2.49400256	0.14350690
F	2.03998181	-2.39324070	0.03518537
C	-0.05300232	1.25686542	-1.56879802
C	-0.69052687	2.50084864	-1.49352031
C	-0.76139785	3.37873953	-2.58056164
C	-0.18164892	3.01040554	-3.80051677
C	0.45866229	1.77272405	-3.91745878
C	0.51149537	0.92602972	-2.80405388
F	-1.25459380	2.90134198	-0.32947945
F	-1.37647672	4.57713948	-2.47341997
F	-0.24749573	3.84382761	-4.86233631
F	1.00449540	1.40866961	-5.10060063
F	1.12772036	-0.28018575	-2.96920852
Pt	-0.56560779	0.47694766	2.74754283
C	1.34623817	1.05714075	3.08324710
C	1.77019232	2.38152948	2.91283858
C	3.10087553	2.78372448	3.08005405
C	4.06651976	1.83848411	3.44032560
C	3.68776477	0.50334090	3.62051336
C	2.34767954	0.14991699	3.44260017
F	0.89527102	3.34132082	2.51860849
F	3.46623482	4.06876031	2.88896381
F	5.35381733	2.20663410	3.60308951
F	4.61613434	-0.41847974	3.95974364
F	2.03661633	-1.17374012	3.62464078
C	-1.24451688	1.98539955	3.88906036
C	-2.23856190	2.87745051	3.45442785
C	-2.75449185	3.89363383	4.26416476
C	-2.27784278	4.03863308	5.57266998
C	-1.29969468	3.16196285	6.05372684
C	-0.80162557	2.16446541	5.20871094
F	-2.72691548	2.79587491	2.19405668
F	-3.69763084	4.74339793	3.80403252
F	-2.77261070	5.00724674	6.37104106
F	-0.86085123	3.28368855	7.32615760
F	0.12191911	1.32107056	5.74534375
O	-0.05892380	-1.30104594	1.68510336
H	0.84803864	-1.56480218	1.93718950
N	-2.10316097	-0.16625291	-0.04870094
C	-2.93082424	-0.28084848	1.02890285
N	-2.56718375	-0.11922609	2.32057184
C	-3.52836898	-0.26393827	3.26098574
C	-4.86084004	-0.56837921	2.94095515
C	-5.25404504	-0.71533155	1.60516431
C	-4.28107640	-0.56923045	0.60653620
C	-4.22670206	-0.61195784	-0.81730766
C	-2.90074128	-0.36131761	-1.15670891
H	-3.20268543	-0.11702039	4.29197796
H	-5.58301864	-0.67397280	3.75222782
H	-6.29529573	-0.93358010	1.35225376
H	-5.04614426	-0.80594750	-1.50509137
H	-2.44729719	-0.31637599	-2.14560115

Table SI 1. Natural charges and HSAB-derived global and local-condensed parameters (in au) for the reaction of N1 or N7 atoms in "aza" with the Pt atom in **7**.

	7	aza	
	Pt	N1	N7
$A = E^N - E^{N+1}$ [(a)]	0.04798	-0.22132	
$I = E^{N-1} - E^N$ [(b)]	0.26343	0.09201	
$\mu = -\frac{1}{2}(I+A)$	-0.15571	0.06466	
$S = 1/(I-A)$	4.64135	3.19144	
$\omega = S \cdot \mu^2$	0.11253	0.01334	
q_n^{N+1}	0.20708	-	-
q_n^{N}	0.39120	-0.58848	-0.49617
q_n^{N-1}	-	-0.40234	-0.42139
$f^+ = q_n^{N+1} - q_n^{N+1}$	-0.18412	-	-
$f^- = q_n^{N} - q_n^{N-1}$	-	-0.18614	-0.07478
$s_\pm = S f^\pm$	-0.85456	-0.59406	-0.23866
$\Delta(s^2)_{kl} = (s_{k+} - s_{l-})^2$		**0.0679**	**0.3793**
$\omega_\pm = \omega f^\pm$	$-2.072 \cdot 10^{-2}$	$-8.258 \cdot 10^{-3}$	$-4.877 \cdot 10^{-3}$
$\Delta(\omega^2)_{kl} = (\omega_{k+} - \omega_{l-})^2$		$\mathbf{1.553 \cdot 10^{-4}}$	$\mathbf{2.510 \cdot 10^{-4}}$

[(a)] Electron affinity; [(b)] Vertical ionization potential