Supporting Information for:

Electrochemistry, Chemical Reactivity, and Time-resolved IR Spectroscopy of Donor-Acceptor Systems [(Q^x)Pt(pap^y)] (Q = substituted *o*-Quinone or *o*-Iminoquinone, pap = Phenylazopyridine)

Naina Deibel,[±] *David Schweinfurth,*[∫] *Stephan Hohloch,*[∫] *Milan Delor,*[//] *Igor V. Sazanovich,*[//] *Michael Towrie,*[£] *Julia A. Weinstein,*[*, //] *and Biprajit Sarkar*[*,∫]

Table S1. Crystallographic data for [**1**]BF_4 and [**2**]PF_6.

	[**1**]BF_4	[**2**]PF_6
Chemical formula	$C_{31}H_{34}BF_4N_4OPt$	$C_{57}H_{55}Cl_2F_6NOP_3Pt$
M_r	760.52	1242.92
Crystal system	monoclinic	triclinic
Space group	Cc	*P*-1
a (Å)	42.720(9)	13.037(2)
b (Å)	5.940(1)	14.066(2)
c (Å)	24.200(5)	15.397(3)
α (°)	90	78.583(7)
β (°)	114.00(3)	82.987(9)
γ (°)	90	70.899(7)
V (Å^3)	5610.0(2)	2610.1(7)
Z	8	2
D_{calc} (g/cm^3)	1.801	1.581
Temperature (K)	100(2)	100(2)
μ (mm^{-1})	5.063	2.945
Crystal size (mm)	0.40 x 0.10 x 0.05	0.35 x 0.23 x 0.19
MoKα	0.71073	0.71073
F(000)	3000	1246
meas./ indep. refl.	22637/ 8236	164155 / 15978
obsvd. [$I > 2\sigma(I)$] refl.	7698	14942
R_{int}	0.0324	0.0295
R[$F^2 > 2\sigma(F^2)$]	0.0283	0.0183
wR (F^2)	0.0780	0.0451
S	1.173	1.070
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.544, -0.918	1.409, -0.800

Table S2. Selected bond lengths (Å) and bond angles (°)

	1[a]	**[1]**BF_4	**[2]**PF_6	**3**[b]
Pt - O1/Pt - O2	1.964(3)	1.976(5)	2.051(1)	1.994(4)/1.966(5)
Pt - N1	1.978(3)	1.890(9)	2.088(1)	-
O1 - C1	1.329(4)	1.227(9)	1.315(2)	1.360(7)
N1 - C2/O2 - C2	1.386(5)	1.31(1)	1.355(2)	1.353(7)
C1 - C2	1.422(5)	1.40(1)	1.439(2)	1.416(8)
C2 - C3	1.407(5)	1.34(2)	1.423(2)	1.379(9)
C3 - C4	1.379(5)	1.35(1)	1.370(2)	1.395(8)
C4 - C5	1.408(5)	1.40(1)	1.433(2)	1.396(9)
C5 - C6	1.388(5)	1.30(1)	1.383(2)	1.385(9)
C6 - C1	1.403(5)	1.42(1)	1.430(2)	1.405(9)
Pt - N2 / Pt - P1	1.962(3)	1.859(6)	2.2584(5)	1.983(5)
Pt - N4 / Pt - P2	1.964(3)	1.989(7)	2.2675(5)	1.966(5)
N2 - N3	1.321(4)	1.25(1)	-	1.307(7)
N3 - C21	1.362(5)	1.36(1)	-	1.390(8)

[a]From reference S1. [b]From reference S2.

	1[a]		**[1]**BF_4		**[2]**PF_6
N1 – Pt – N2	108.1 (1)	**O1 – Pt – N2**	96.1(3)	**O1 – Pt – N1**	79.14(5)
N2 – Pt – N4	77.6(1)	**O1 – Pt – N1**	82.0(3)	**N1 – Pt – P2**	97.17(4)
N4 – Pt – O1	93.7(2)	**N1 – Pt – N4**	102.6(3)	**P2 – Pt – P1**	94.79(2)
N1 – Pt – O1	80.9(1)	**N4 – Pt – N2**	79.6(3)	**P1 – Pt – O1**	88.71(3)

[a]From reference S1.

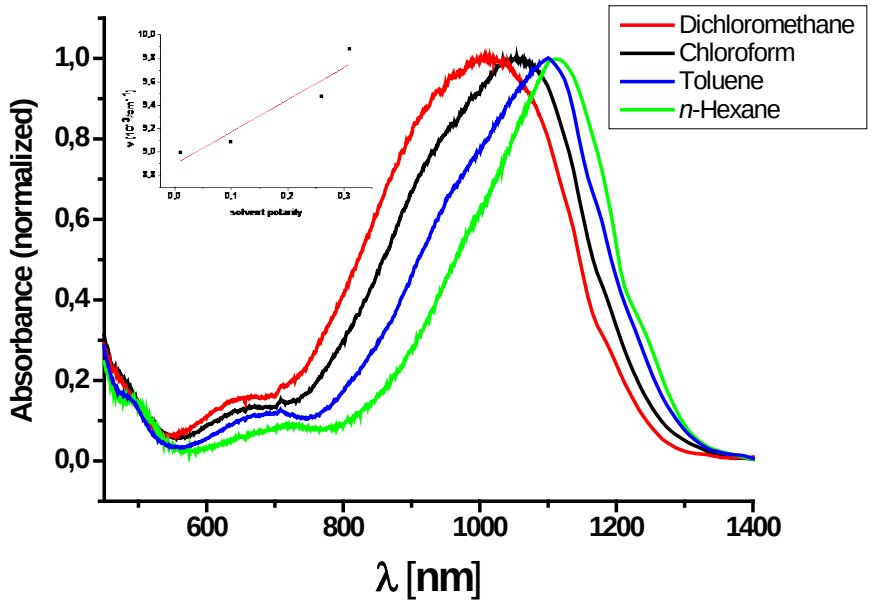

Figure S1. Normalized absorption spectra of **3** in various solvents.

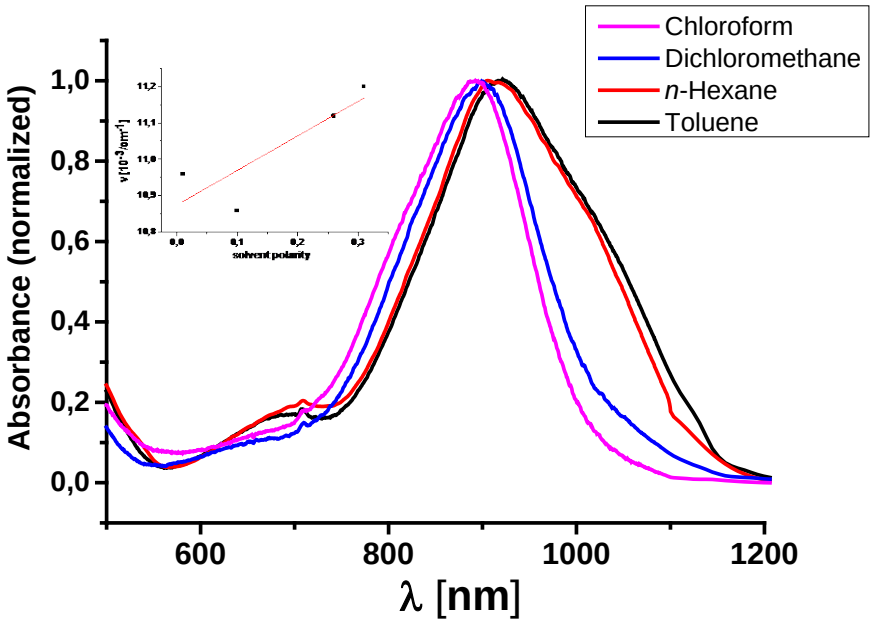

Figure S2. Normalized absorption spectra of **1** in various solvents.

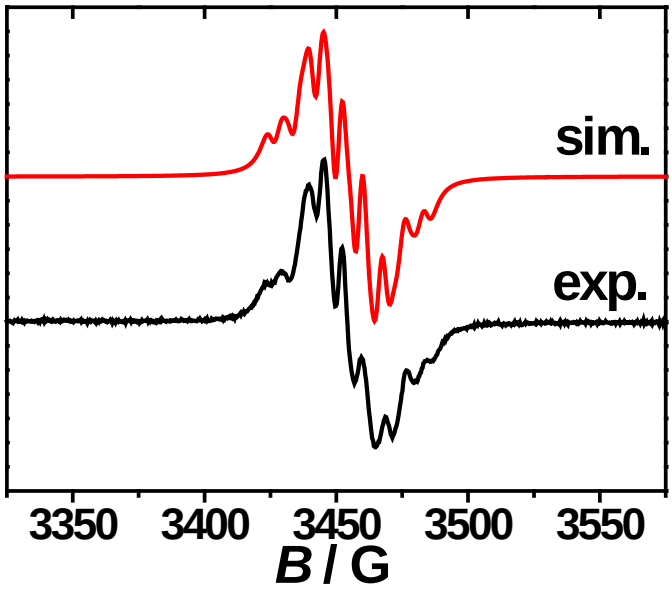

Figure S3. EPR spectrum of the reaction product between $\mathbf{1}^{\bullet+}$ and PPh_3 in CH_2Cl_2 at 295 K recorded immediately after mixing stoichiometric amounts of the two reactants (bottom) together with simulation (top). g = 1.998, $a(^{195}Pt)$ = 32 G, $a(^{14}N)$ = 7.6 G, $a(^{1}H)$ = 4.6 G, $a(^{31}P)$ = 7 G.

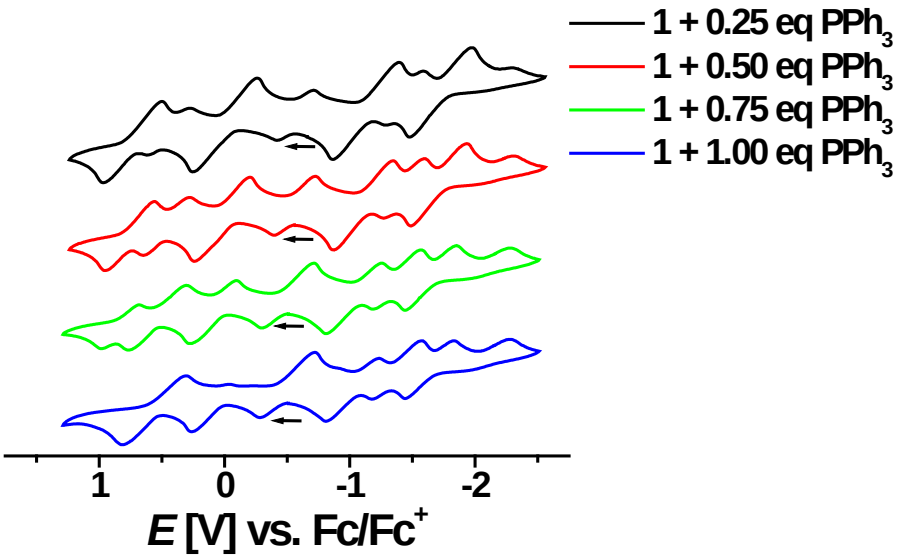

Figure S4. Cyclic voltammogram of **1** in CH_2Cl_2 / 0.1 M Bu_4NPF_6 at -40 °C in the presence of various amounts of CH_2Cl_2.

Table S3. UV-vis-NIR data of the complexes in their various redox forms[a]

	λ [nm] (ε [10^3 M^{-1} · cm^{-1}])
[1]^0	241 (17.6); 326 (12.1); 392 (5.4); 457 (4.6); 679 sh; 897 (20.9)
[1]$^+$	238 (22.5); 305 (11.9); 338 sh; 415 (10.5); 535 (9.4); 1114 (3.8)
[2]^0	229 (83.8); 340 (12.3); 400 sh
[2]$^+$	229 (85.9); 265 sh; 334 (18.5); 421 (5.8); 469 (6.7); 908 (2.0)
[2]$^{2+}$	227 (83.8); 270 sh; 369 sh; 593 (1.8)
[3]^{0,b}	319(8.4), 390(9.3), 477 (2.1), 650 (1.7), 970(9.5)

[a] From OTTLE spectroelectrochemistry in CH_2Cl_2/0.1 M Bu_4NPF_6. [b] From ref. 7b.

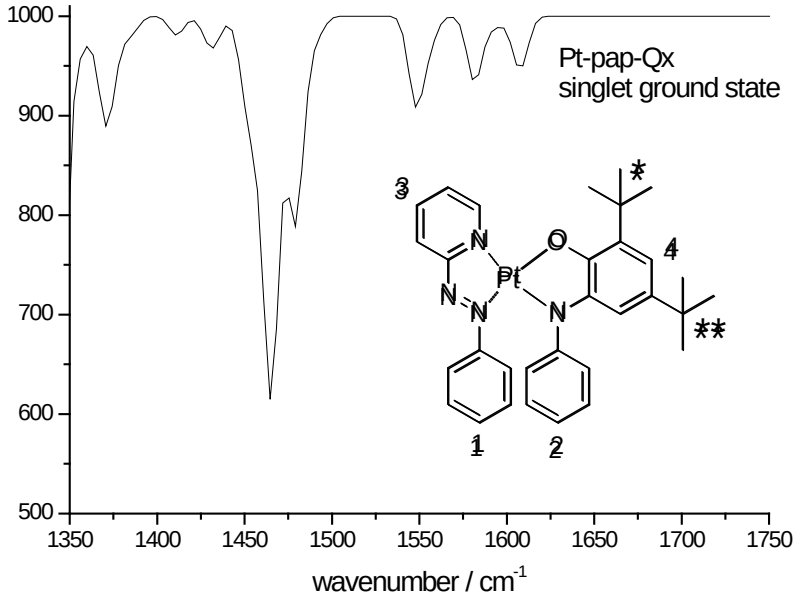

Figure S5. Simulated IR spectrum of the singlet ground state of **1b** in CH_2Cl_2. The corresponding band assignment is given in Table S4.

Table S4. Band assignments corresponding to Figure S5 and inset.

Mode	Frequency	T^^2	assignments
165	1463	140	All tButyl + phenyl bending modes. **Mainly * and 3**

166	1466	225	Same, all involved equally
168	1478	180	**Mainly 1 and 3**
171	1548	88	**Mainly 4,** strong amplitude, coupled to 3
173	1582	66	**Mainly 4,** coupled to 2
177	1607	24	**Mainly 2 and 3**, coupled to 4
178	1609	27	**Mainly 3,** coupled to 1 and 2

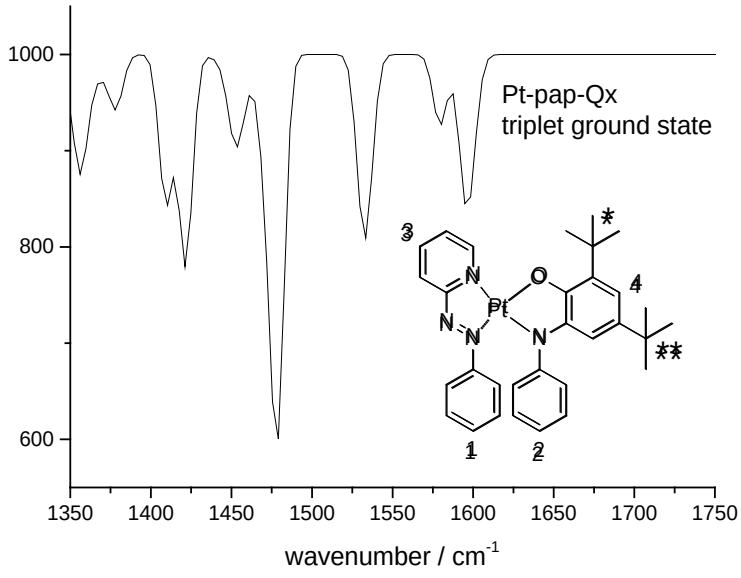

Figure S6. Simulated IR spectrum of the triplet ground state of **1b** in CH_2Cl_2. The corresponding band assignement is given in Table S5.

Table S5. Band assignments corresponding to Figure S6 and inset.

Mode	Frequency	T^^2	Assignments
151	1409	155	**Mainly 4**, affecting O, N and *
152	1422	219	**As above**, different bending modes
161	1452	42	**Mostly * and ****
162	1453	26	**Mostly ** and 1**
169	1477	158	**Mostly 1, 2 and 3**
170	1479	246	**As above**

171	1531	126	**Mostly 4**
172	1535	86	**Mostly 3**
173	1579	72	**Mostly 4**
176	1595	115	**Mostly 3**, coupled to 2
177	1599	61	**Mostly 1**, coupled to 3

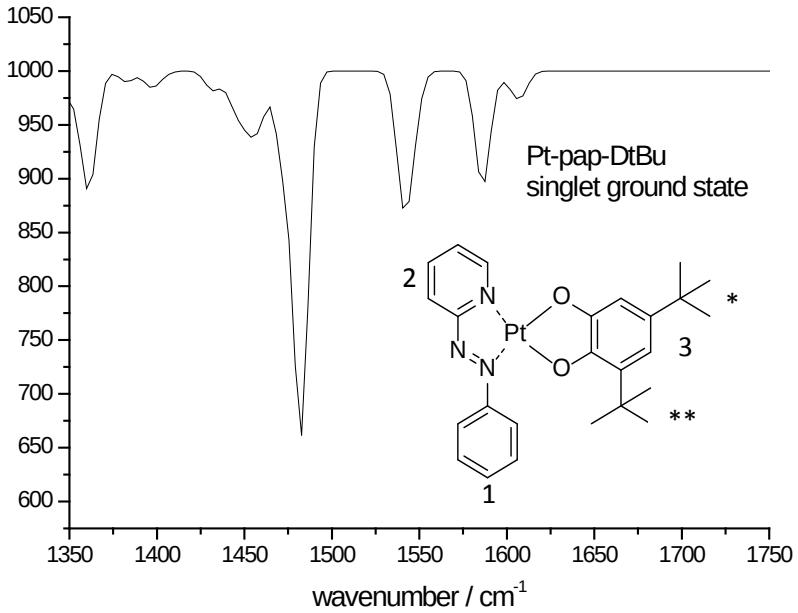

Figure S7. Simulated IR spectrum of the singlet ground state of **3** in CH_2Cl_2. The corresponding band assignement is given in Table S6.

Table S6. Band assignments corresponding to Figure S7 and inset.

Mode	Frequency	T^^2	Assignments
135	1451	18	All bending modes, **mainly 1 and ****
136	1453	10	**Mainly 3, * and **** with some 1
137	1455	17	**Mostly ***
143	1482	323	**Mainly 1 and 2,** some 3 and **
145	1541	113	**Mainly 2 and 3**
146	1546	38	**Mainly 2 and 3**
147	1586	107	**Mainly 3**
150	1608	22	**Mainly 2, some 1**

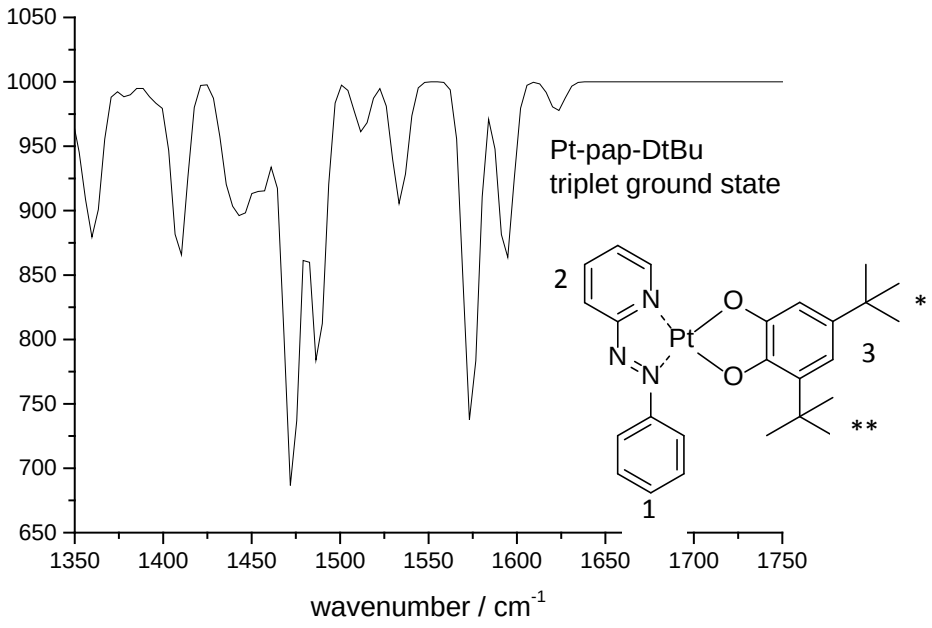

Figure S8. Simulated IR spectrum of the triplet ground state of **3** in CH_2Cl_2. The corresponding band assignement is given in Table S7.

Table S7. Band assignments corresponding to Figure S8 and inset.

Mode	Frequency	T^^2	Assignments
127	1409	139	**Mainly 3,** affecting **, * and O
142	1473	291	**Mainly 2 and 1**
144	1487	222	**As above, 1 more than 2**
146	1534	95	**Mainly 2**
147	1574	267	**Mostly 3**
149	1594	141	**Mostly 2**

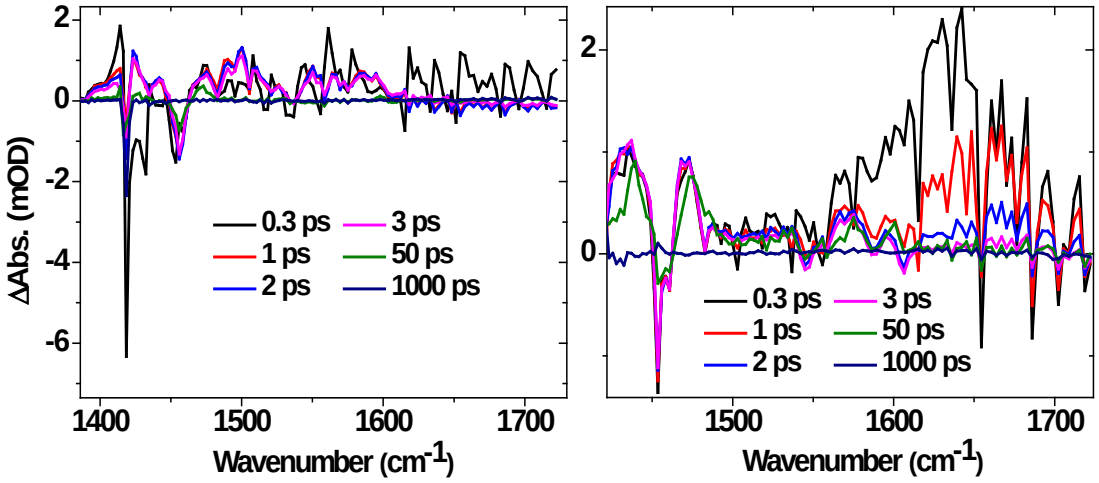

Figure S9. Early-time TRIR spectra following 400 nm excitation for **1b** (left) and **3** (right). The 0.3 – 2 ps traces show large signals in the 1600 cm^{-1} region associated with vibrationally excited water molecules that are hydrogen-bonded to the compounds. It should be noted that compounds **1b** and **3** are expected to have strong affinity to water, through H-bonding to one (^{O,N}Q) or two (^{O,O}Q) oxygen atoms. This leads to water molecules being associated in a "supermolecule" if even traces of moisture are present. This susceptibility to water can give rise to early-time effects in the TRIR spectra as some of the excitation energy is rapidly distributed to H-bonded water molecules which give strong signals in the fingerprint IR region investigated, and which decay with lifetimes of 0.5 – 1 ps as vibrationally excited water molecules cool down. Such an interpretation is further supported by the fact that these early-time effects have not been observed in our experiments using the same set-up and related Pt(II) compounds but without O-donor atoms – such as Pt(II) diimine acetylides[S3] – and is more pronounced for **3** than for **1b**..

References:

(S1) Deibel, N.; Schweinfurth, D.; Hohloch, S.; Fiedler, J.; Sarkar, B., *Chem. Commun.*, **2012**, *48*, 2388.

(S2) Sarkar, B.; Huebner, R.; Pattacini, R.; Hartenbach, I., *Dalton Trans.*, **2009**, 4653.

(S3) Adams, C. J.; Fey, N.; Harrison, Z. A.; Sazanovich, I. V; Towrie, M.; Weinstein, J. A. *Inorg. Chem.* **2008**, *47*, 8242.

Optimized structure (BP86) of **1** in the singlet state:

C	3.452208	4.910924	6.480684
C	2.042023	5.144147	6.460672
C	1.308189	5.151585	5.229976
C	3.384620	4.815974	3.985036
C	4.240259	4.870359	7.807830
C	5.735564	4.547174	7.588849
H	6.252374	4.513689	8.568080
H	6.245073	5.315466	6.974945
H	5.882346	3.562143	7.103914
C	3.654563	3.771656	8.735264
H	4.206835	3.747298	9.696586
H	3.746487	2.772366	8.266022
H	2.586322	3.947730	8.953495
C	4.155681	6.255461	8.504875
H	4.703541	6.234624	9.468958
H	3.109240	6.546407	8.705155
H	4.611546	7.041794	7.871638
C	4.186789	4.661854	2.673934
C	3.293184	4.782608	1.420288
H	3.909748	4.671092	0.506750
H	2.791035	5.767856	1.363234
H	2.512890	3.997327	1.390433
C	5.272670	5.768283	2.598787
H	5.864251	5.669936	1.666072
H	5.978775	5.714564	3.449264
H	4.812719	6.775683	2.608521
C	4.869949	3.268397	2.647051
H	5.457931	3.141242	1.715519
H	4.117001	2.457288	2.690587
H	5.561144	3.129027	3.500114
C	-0.869605	5.621093	4.251013
C	-1.551092	6.853080	4.144483

H	-1.429979	7.593120	4.946247
C	-2.360404	7.121248	3.028717
H	-2.885506	8.083740	2.960408
C	-2.494012	6.169956	2.001887
H	-3.126443	6.382040	1.129418
C	-1.818026	4.940295	2.104554
H	-1.927743	4.184012	1.315023
C	-1.014293	4.662747	3.221464
H	-0.511006	3.691853	3.317466
C	-2.336158	6.352450	9.442480
C	-2.746543	6.847078	10.710874
H	-3.809440	7.070488	10.857434
C	-1.800373	7.022411	11.712896
H	-2.099754	7.401164	12.698473
C	-0.440448	6.700597	11.449836
H	0.331416	6.818129	12.219281
C	-0.081457	6.229729	10.191720
H	0.948881	5.973634	9.919368
C	-3.539068	5.134796	6.385879
C	-3.211495	3.971814	5.659713
H	-2.241299	3.490706	5.835795
C	-4.141780	3.426787	4.761743
H	-3.885827	2.513395	4.208561
C	-5.396305	4.035201	4.578950
H	-6.121259	3.604786	3.875071
C	-5.719633	5.197004	5.306191
H	-6.696289	5.680236	5.166650
C	-4.802215	5.745050	6.212580
H	-5.043680	6.642250	6.793738
C	2.001848	5.027142	3.996987
H	1.441020	5.108048	3.062098
C	4.071036	4.742900	5.233064
H	5.150996	4.560721	5.213073
N	-0.056970	5.364766	5.394174

N	-0.998748	6.059147	9.200329
N	-3.214157	6.093039	8.451128
N	-2.614989	5.638717	7.350629
O	1.334757	5.413806	7.564514
Pt	-0.631739	5.580721	7.300658

Optimized structure (BP86) of **1** in the triplet state:

C	3.471343	4.881297	6.491196
C	2.053267	5.105009	6.488043
C	1.319577	5.143181	5.239858
C	3.405204	4.893989	3.985280
C	4.260264	4.787217	7.814744
C	5.758829	4.492555	7.578941
H	6.276518	4.418565	8.555244
H	6.259727	5.295670	7.003443
H	5.918172	3.533116	7.048525
C	3.687340	3.637241	8.686871
H	4.240746	3.573309	9.645386
H	3.791493	2.662817	8.170223
H	2.617675	3.790306	8.914432
C	4.159983	6.135943	8.578000
H	4.708002	6.072379	9.539809
H	3.111144	6.405788	8.793259
H	4.608915	6.957218	7.985396
C	4.220069	4.820354	2.677213
C	3.333082	4.985854	1.424269
H	3.957726	4.928258	0.511463
H	2.815450	5.964600	1.409678
H	2.566284	4.190378	1.350444
C	5.284804	5.949994	2.667648
H	5.884967	5.907836	1.736522
H	5.986466	5.868707	3.519644
H	4.805695	6.946924	2.721406

C	4.929947	3.442546	2.589743
H	5.529063	3.374541	1.659411
H	4.193034	2.615837	2.583283
H	5.616813	3.272558	3.440813
C	-0.864031	5.411041	4.233414
C	-1.671466	6.556354	4.058746
H	-1.639358	7.347310	4.818825
C	-2.491175	6.673822	2.926324
H	-3.111443	7.570990	2.799285
C	-2.526994	5.648567	1.963598
H	-3.176650	5.740417	1.083077
C	-1.735163	4.499352	2.141794
H	-1.769583	3.686063	1.403904
C	-0.907585	4.376828	3.268593
H	-0.307754	3.470802	3.424690
C	-2.303664	6.492820	9.423163
C	-2.670111	7.047913	10.682950
H	-3.700250	7.399531	10.809927
C	-1.728886	7.117083	11.704519
H	-2.006770	7.540018	12.678934
C	-0.411605	6.634402	11.484503
H	0.352940	6.669577	12.268525
C	-0.091645	6.112925	10.230384
H	0.907605	5.737902	9.979595
C	-3.600136	5.305363	6.394572
C	-3.330863	4.143542	5.633769
H	-2.382919	3.615169	5.793421
C	-4.286138	3.654906	4.731979
H	-4.068449	2.744280	4.158005
C	-5.519369	4.313961	4.570831
H	-6.264844	3.929282	3.861967
C	-5.792237	5.466738	5.334296
H	-6.753187	5.987230	5.218690
C	-4.849944	5.959941	6.245414

H	-5.056986	6.848356	6.852378
C	2.024934	5.079991	4.001521
H	1.463079	5.196041	3.070843
C	4.088585	4.774851	5.239928
H	5.171299	4.610267	5.213260
N	-0.038753	5.307627	5.385918
N	-0.998975	6.044898	9.228294
N	-3.189424	6.332579	8.423469
N	-2.651189	5.753912	7.336092
O	1.361234	5.302520	7.596797
Pt	-0.636548	5.544695	7.320722

Optimized structure (BP86) of **1**$^{+}$ in the dublet state:

C	3.461915	4.908837	6.493926
C	2.047059	5.141493	6.476059
C	1.303920	5.161405	5.226814
C	3.374568	4.878978	3.975295
C	4.257044	4.832785	7.813854
C	5.749267	4.515968	7.567488
H	6.275218	4.453601	8.539012
H	6.255816	5.302931	6.975578
H	5.893271	3.544123	7.056318
C	3.677154	3.705558	8.711186
H	4.247447	3.647975	9.658785
H	3.757140	2.720422	8.211947
H	2.614798	3.875352	8.962084
C	4.177780	6.200115	8.546726
H	4.742165	6.150804	9.498502
H	3.136877	6.488013	8.779108
H	4.624273	7.006053	7.932648
C	4.194307	4.777922	2.677290
C	3.314942	4.924901	1.417362
H	3.945602	4.848776	0.511466

H	2.804076	5.906604	1.378164
H	2.548300	4.128661	1.348791
C	5.263940	5.905021	2.662450
H	5.865802	5.841699	1.735127
H	5.965859	5.833461	3.514935
H	4.791752	6.905830	2.694235
C	4.897926	3.393422	2.627176
H	5.497902	3.308825	1.700272
H	4.160141	2.567913	2.631319
H	5.586614	3.236974	3.479159
C	-0.880759	5.459898	4.237707
C	-1.634500	6.638816	4.053700
H	-1.558100	7.446649	4.793073
C	-2.443618	6.777576	2.915606
H	-3.014393	7.703395	2.767069
C	-2.517948	5.741577	1.965996
H	-3.153337	5.853962	1.078026
C	-1.777160	4.560548	2.158177
H	-1.840005	3.744835	1.425846
C	-0.958372	4.415013	3.288370
H	-0.393226	3.488454	3.453220
C	-2.297398	6.376611	9.466247
C	-2.711956	6.872871	10.720168
H	-3.767433	7.131726	10.859873
C	-1.762716	7.008943	11.737875
H	-2.058451	7.391290	12.722574
C	-0.423181	6.641644	11.485564
H	0.345644	6.724494	12.262288
C	-0.066817	6.161496	10.220845
H	0.956387	5.867693	9.960968
C	-3.566378	5.268711	6.376761
C	-3.303935	4.085901	5.654731
H	-2.377806	3.529937	5.845513
C	-4.265376	3.604662	4.755099

H	-4.079160	2.669473	4.212283
C	-5.467543	4.309365	4.558647
H	-6.214084	3.931767	3.847899
C	-5.717733	5.496188	5.276986
H	-6.654039	6.047419	5.121230
C	-4.777961	5.975051	6.197092
H	-4.960736	6.889368	6.773192
C	1.999257	5.072775	3.982969
H	1.438797	5.172191	3.050143
C	4.062182	4.776019	5.240596
H	5.142802	4.603035	5.208985
N	-0.043065	5.339957	5.387904
N	-0.983039	6.033824	9.232156
N	-3.190237	6.143898	8.454557
N	-2.628318	5.688443	7.368492
O	1.346337	5.380770	7.570227
Pt	-0.628323	5.563182	7.315369

Optimized structure (BP86) of **1**$^{-}$ in the dublet state:

C	3.453062	4.885893	6.470308
C	2.048264	5.133356	6.444427
C	1.325657	5.139776	5.206834
C	3.434369	4.787006	3.987244
C	4.222230	4.848126	7.810584
C	5.719770	4.513293	7.624338
H	6.218115	4.482820	8.614823
H	6.244690	5.273256	7.012131
H	5.867539	3.524820	7.145570
C	3.614517	3.761237	8.737359
H	4.135833	3.749213	9.717993
H	3.721081	2.756977	8.280492
H	2.539346	3.944335	8.911533
C	4.135502	6.236515	8.500124

H	4.653162	6.218366	9.482777
H	3.083699	6.533129	8.660014
H	4.617674	7.012646	7.872614
C	4.240762	4.627837	2.676573
C	3.355224	4.754820	1.417364
H	3.974464	4.637543	0.504430
H	2.858319	5.742681	1.361817
H	2.566168	3.978418	1.389326
C	5.336695	5.723980	2.599215
H	5.937097	5.622062	1.670093
H	6.031060	5.667474	3.459321
H	4.880908	6.733552	2.607023
C	4.916589	3.231087	2.643922
H	5.511625	3.098357	1.715209
H	4.155287	2.427283	2.683997
H	5.596521	3.086245	3.505286
C	-0.848763	5.648727	4.216038
C	-1.650329	6.817986	4.190093
H	-1.614499	7.485482	5.060958
C	-2.469631	7.108227	3.089474
H	-3.084532	8.019760	3.101705
C	-2.508010	6.247373	1.976448
H	-3.151193	6.476172	1.115020
C	-1.724986	5.078370	1.992304
H	-1.762909	4.379268	1.143565
C	-0.912135	4.776872	3.096506
H	-0.345525	3.837111	3.121302
C	-2.340312	6.454693	9.398974
C	-2.713113	6.996784	10.672177
H	-3.762377	7.282718	10.814846
C	-1.764255	7.135004	11.673597
H	-2.051126	7.546634	12.651805
C	-0.416500	6.736590	11.428843
H	0.360577	6.828863	12.197064

C	-0.089489	6.228573	10.173797
H	0.927507	5.918229	9.903576
C	-3.581501	5.140674	6.420771
C	-3.201951	4.078819	5.560922
H	-2.171394	3.707878	5.615186
C	-4.134051	3.495834	4.692570
H	-3.811958	2.673092	4.038388
C	-5.469850	3.942891	4.659790
H	-6.197586	3.481815	3.977027
C	-5.856606	4.988149	5.522318
H	-6.895593	5.351138	5.513537
C	-4.935314	5.578883	6.396808
H	-5.234050	6.384517	7.076235
C	2.044772	5.010953	3.992426
H	1.501375	5.107984	3.048548
C	4.104478	4.706562	5.231529
H	5.183441	4.510750	5.231911
N	-0.051008	5.370772	5.345779
N	-1.003401	6.089264	9.180632
N	-3.222116	6.242716	8.422989
N	-2.647210	5.691678	7.312702
O	1.348798	5.412517	7.558721
Pt	-0.635727	5.601426	7.277478