

Electronic supplementary information

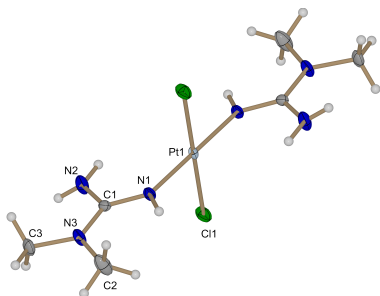


Fig. S1 Thermal ellipsoid view of *trans*-1 with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability.

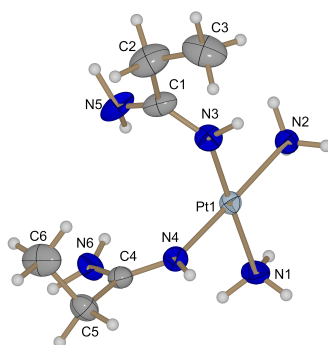
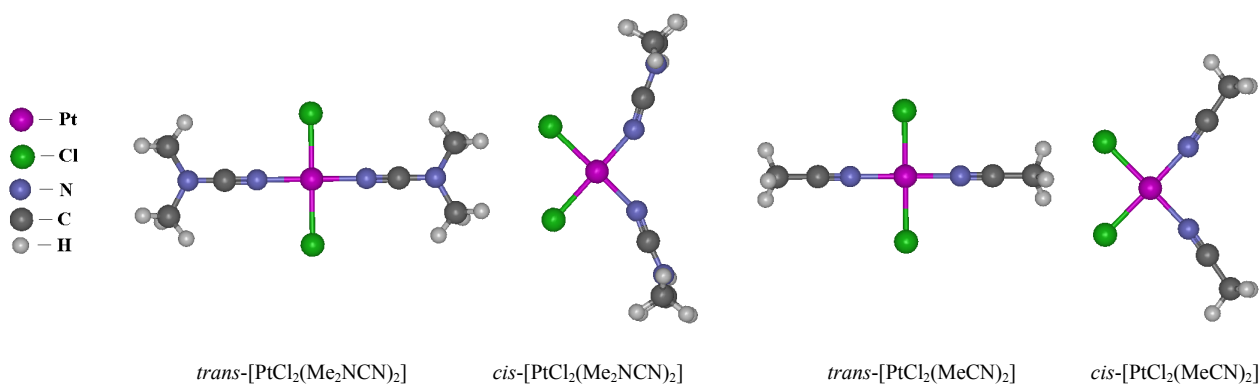
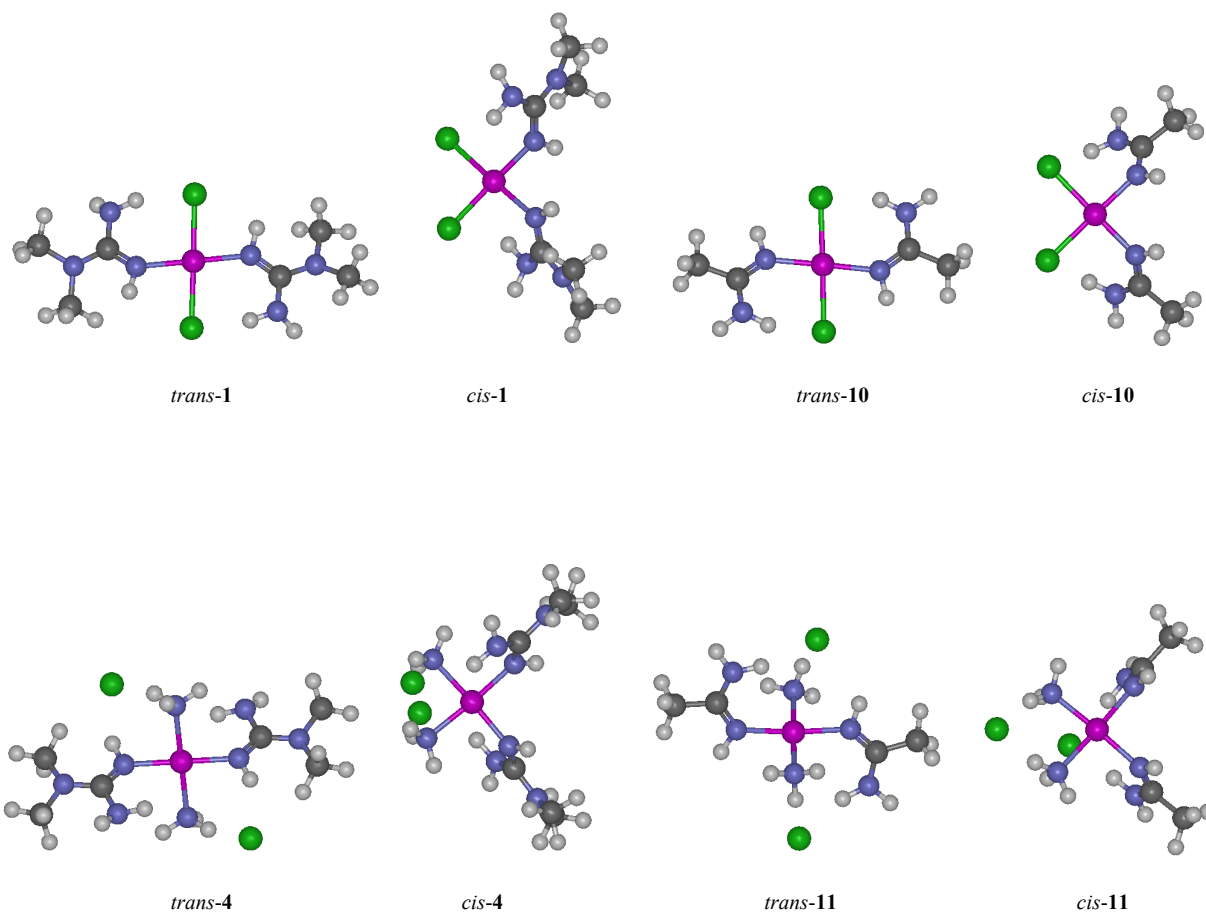


Fig. S2 Thermal ellipsoid view of *cis*-7²⁺ with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. The counter anions have been omitted for clarity.





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Fig. S3 General views of the equilibrium geometries.

Table S1 Selected calculated bond lengths (Å).

	<i>cis</i> -[PtCl ₂ (MeCN) ₂]	<i>trans</i> -[PtCl ₂ (MeCN) ₂]	<i>cis</i> -[PtCl ₂ (Me ₂ NCN) ₂]	<i>trans</i> -[PtCl ₂ (Me ₂ NCN) ₂]
Pt–Cl	2.321	2.369	2.329	1.375
Pt–N	2.004	1.964	2.015	1.968
N≡C	1.155	1.152	1.167	1.160
C–C	1.457	1.456		
C–N(Me) ₂			1.317	1.319
N–C _{Me}			1.471	1.469
	<i>cis-1</i>	<i>trans-1</i>	<i>cis-10</i>	<i>trans-10</i>
Pt–Cl	2.357	2.388, 2.392	2.364	2.390
Pt–N	2.063	2.055, 2.057	2.057	2.048, 2.050
N=C	1.311	1.309, 1.311	1.303	1.302, 1.303
C–C			1.509	1.510, 1.511
C–N(Me) ₂	1.368	1.377, 1.379		
N–C _{Me}	1.454, 1.460	1.455–1.461		
CN _{NH₂}	1.377	1.366, 1.368	1.350	1.343, 1.348
	<i>cis-4</i>	<i>trans-4</i>	<i>cis-11</i>	<i>trans-11</i>
Pt–N _{NH₃}	2.081	2.086	2.081	2.077, 2.091
Pt–N	2.055	2.051	2.054	2.040, 2.048
N=C	1.322	1.309	1.311	1.310, 1.313
C–C			1.512	1.511, 1.512
C–N(Me) ₂	1.373	1.365		
N–C _{Me}	1.455, 1.460	1.462, 1.467		

	<i>cis</i> -[PtCl ₂ (MeCN) ₂]	<i>trans</i> -[PtCl ₂ (MeCN) ₂]	<i>cis</i> -[PtCl ₂ (Me ₂ NCN) ₂]	<i>trans</i> -[PtCl ₂ (Me ₂ NCN) ₂]
C–N _{NH₃}	1.357	1.385	1.336	1.337, 1.338

Table S2 Gas-phase total energies (E_g) and enthalpies (H_g) and total energies in the CH₂Cl₂ solution (E_s) calculated using the corresponding basis set (in Hartree).

	$E_g(6-31G(d))$	$E_g(6-311+G(d,p))$	$E_s(6-311+G(d,p))$	$H_g(6-31G(d))$
NH ₃	–56.547948	–56.582942	–56.587762	–56.509618
<i>trans</i> -[PtCl ₂ (Me ₂ NCN) ₂]	–1494.709721	–1494.900612	–1494.918997	–1494.500196
<i>cis</i> -[PtCl ₂ (Me ₂ NCN) ₂]	–1494.700666	–1494.892215	–1494.914016	–1494.491530
<i>trans</i> -[PtCl ₂ (MeCN) ₂]	–1305.410811	–1305.547496	–1305.558393	–1305.298316
<i>cis</i> -[PtCl ₂ (MeCN) ₂]	–1305.401055	–1305.538939	–1305.555094	–1305.288899
<i>trans</i> - 1	–1607.919388	–1608.162080	–1608.179089	–1607.623375
<i>cis</i> - 1	–1607.903340	–1608.145470	–1608.170774	–1607.607608
<i>trans</i> - 4	–1721.049015	–1721.347043	–1721.377360	–1720.669485
<i>cis</i> - 4	–1721.048430	–1721.344654	–1721.378068	–1720.669264
<i>trans</i> - 10	–1418.608071	–1418.798608	–1418.814277	–1418.409360
<i>cis</i> - 10	–1418.590062	–1418.780496	–1418.806408	–1418.391648
<i>trans</i> - 11	–1531.738665	–1531.983351	–1532.012024	–1531.456823
<i>cis</i> - 11	–1531.741829	–1531.986868	–1532.018634	–1531.460036

Table S3 Reaction energies and enthalpies for the gas phase (ΔE_g and ΔH_g) and the CH₂Cl₂ solution (ΔE_s and ΔH_s , in parentheses) calculated using the corresponding basis set (in kcal/mol).

Reaction	$\Delta E_g(6-31G(d))$	$\Delta E_g(\Delta E_s)$ (6-311+G(d,p))	$\Delta H_g(6-31G(d))$ ($\Delta H_s(6-311+G(d,p))$)
<i>cis</i> -[PtCl ₂ (Me ₂ NCN) ₂] + 2NH ₃ → <i>cis</i> - 1	–67.0	–54.8 (–51.0)	–60.8 (–44.8)
<i>trans</i> -[PtCl ₂ (Me ₂ NCN) ₂] + 2NH ₃ → <i>trans</i> - 1	–71.4	–60.0 (–53.1)	–65.2 (–46.9)
<i>cis</i> - 1 + 2NH ₃ → <i>cis</i> - 4	–30.9	–20.9 (–19.9)	–26.6 (–15.7)
<i>trans</i> - 1 + 2NH ₃ → <i>trans</i> - 4	–21.2	–12.0 (–14.3)	–16.9 (–10.0)
<i>cis</i> -[PtCl ₂ (MeCN) ₂] + 2NH ₃ → <i>cis</i> - 10	–58.4	–47.5 (–47.6)	–52.4 (–41.5)
<i>trans</i> -[PtCl ₂ (MeCN) ₂] + 2NH ₃ → <i>trans</i> - 10	–63.6	–53.5 (–50.4)	–57.6 (–44.4)
<i>cis</i> - 10 + 2NH ₃ → <i>cis</i> - 11	–35.1	–25.4 (–23.0)	–30.8 (–18.8)
<i>trans</i> - 10 + 2NH ₃ → <i>trans</i> - 11	–21.8	–11.8 (–14.0)	–17.7 (–9.9)
<i>trans</i> -[PtCl ₂ (MeCN) ₂] → <i>cis</i> -[PtCl ₂ (MeCN) ₂]	+6.1	+5.4 (+2.1)	+5.9 (+1.9)
<i>trans</i> -[PtCl ₂ (Me ₂ NCN) ₂] → <i>cis</i> -[PtCl ₂ (Me ₂ NCN) ₂]	+5.7	+5.3 (+3.1)	+5.4 (+2.9)
<i>trans</i> - 1 → <i>cis</i> - 1	+10.1	+10.4 (+5.2)	+9.9 (+5.0)
<i>trans</i> - 4 → <i>cis</i> - 4	+0.4	+1.5 (–0.4)	+0.1 (–0.7)
<i>trans</i> - 10 → <i>cis</i> - 10	+11.3	+11.4 (+4.9)	+11.1 (+4.8)
<i>trans</i> - 11 → <i>cis</i> - 11	–2.0	–2.2 (–4.2)	–2.0 (–4.2)

Table S4 Calculated Cartesian atomic coordinates for the equilibrium structures.

	x	y	z		x	y	z
		<i>trans</i> -[PtCl ₂ (Me ₂ NCN) ₂]				<i>cis</i> -[PtCl ₂ (Me ₂ NCN) ₂]	
Pt	0.000399	0.000226	0.071167	Pt	−0.367647	0.016657	0.367579
Cl	−1.541505	1.805954	0.069645	Cl	−1.433647	1.740912	1.514740
N	−1.495881	−1.277409	0.082216	N	0.540663	−1.492333	−0.611742
C	−2.378177	−2.030510	0.076563	C	0.751677	−2.609545	−0.874878
N	−3.380686	−2.886374	0.121729	N	1.057489	−3.838480	−1.238169
Cl	1.542296	−1.805528	0.063730	Cl	−1.591143	−1.602672	1.510435
N	1.496703	1.277831	0.060495	N	0.678609	1.436253	−0.607979
C	2.378854	2.030851	0.040369	C	0.991428	2.529949	−0.868664
N	3.381681	2.887092	0.069686	N	1.409503	3.726287	−1.228824
C	4.737935	2.390796	−0.197458	C	0.543637	4.534399	−2.101234
C	3.103267	4.305100	−0.192686	C	2.311802	4.452138	−0.321700
C	−4.739727	−2.391773	−0.134014	C	1.893538	−4.644970	−0.335707

C	-3.105227	-4.306241	-0.133484
H	4.810658	1.349213	0.119689
H	5.448342	2.990212	0.379499
H	4.986012	2.463115	-1.264386
H	3.808081	4.911200	0.384151
H	2.086770	4.539162	0.127802
H	3.210751	4.541809	-1.259232
H	-4.808784	-1.347858	0.176204
H	-5.443854	-2.986735	0.455136
H	-4.999528	-2.471911	-1.197585
H	-3.803321	-4.908189	0.455755
H	-2.085100	-4.538007	0.176970
H	-3.224938	-4.550639	-1.196989

trans-[PtCl₂(MeCN)₂]

Pt	0.000000	-0.000123	0.000406
Cl	0.000580	-2.369298	-0.000372
N	1.963687	0.000371	0.000128
C	3.115923	0.000713	-0.000400
C	4.571627	0.001012	-0.001937
Cl	-0.000581	2.369216	0.000648
N	-1.963687	-0.000448	0.000370
C	-3.115922	-0.000225	-0.000422
C	-4.571627	0.000147	-0.001929
H	-4.942763	-0.730046	-0.727820
H	-4.942380	0.994205	-0.270334
H	-4.944984	-0.264581	0.992321
H	4.942459	0.994867	-0.270978
H	4.942669	-0.729676	-0.727380
H	4.944998	-0.263121	0.992466

trans-**1**

Pt	-0.004269	-0.023400	-0.121717
Cl	-0.048172	-2.394859	-0.401672
Cl	0.020409	2.353930	0.144740
N	-2.030741	0.267423	-0.301623
C	-3.098665	-0.379615	0.097072
N	-4.301456	0.257493	0.305536
C	-4.359659	1.710748	0.368997
C	-5.571195	-0.406325	0.022061
H	-3.478660	2.103018	0.882370
H	-5.247158	1.998633	0.941217
H	-4.432232	2.175876	-0.626918
H	-6.243493	-0.347366	0.887067
H	-5.395677	-1.452374	-0.227343
H	-6.069558	0.072152	-0.833139
H	-2.212567	1.217115	-0.607511
N	-3.080966	-1.729305	0.305207
H	-2.173268	-2.172209	0.153031
H	-3.592621	-2.066923	1.109892
N	2.020789	-0.331220	0.067189
C	3.107652	0.398076	0.028800
N	4.338840	-0.113976	0.379928
C	4.426360	-1.420071	1.015673
C	5.561246	0.338443	-0.280844
H	3.629491	-1.533480	1.755018
H	5.386622	-1.488891	1.535647
H	4.367979	-2.250744	0.294608
H	6.320355	0.621604	0.458635
H	5.345908	1.192914	-0.921547

C	0.117870	-4.562929	-2.107748
H	-0.007902	3.875532	-2.773737
H	1.175071	5.202764	-2.693840
H	-0.167243	5.128702	-1.514013
H	2.939337	5.120692	-0.918223
H	2.949006	3.737957	0.202204
H	1.747343	5.039597	0.412907
H	2.595325	-3.992676	0.186377
H	2.455106	-5.366989	-0.935653
H	1.280894	-5.179742	0.400546
H	0.683185	-5.285453	-2.703546
H	-0.373808	-3.855529	-2.777375
H	-0.642027	-5.090498	-1.518171

cis-[PtCl₂(MeCN)₂]

Pt	-0.427342	-0.006119	0.014318
Cl	-2.070983	1.631986	0.060797
N	0.955266	-1.456497	-0.024413
C	1.641085	-2.385845	-0.042525
C	2.480089	-3.576493	-0.064430
Cl	-2.022826	-1.690667	0.076278
N	0.912662	1.483288	-0.038111
C	1.571292	2.431890	-0.065023
C	2.375479	3.646071	-0.098193
H	2.980349	3.675704	-1.009822
H	3.037370	3.686607	0.772481
H	1.713717	4.517893	-0.082350
H	3.148405	-3.585678	0.802220
H	3.079757	-3.601207	-0.979638
H	1.844130	-4.466868	-0.032188

cis-**1**

Pt	-0.936965	0.075645	-0.210621
Cl	-2.291213	1.802511	-1.069678
Cl	-2.774110	-1.393623	-0.068522
N	0.702882	1.321683	-0.324881
H	1.475392	0.993063	-0.891050
N	0.287288	-1.401464	0.547103
H	0.786502	-1.175167	1.398505
N	-0.039987	3.003907	1.100703
H	-0.806162	2.347681	1.242171
H	-0.401562	3.936425	0.929175
N	1.789094	3.410511	-0.303527
N	-0.026795	-2.998898	-1.115335
H	-0.550105	-2.238734	-1.546571
H	-0.564744	-3.858810	-1.145515
N	0.946863	-3.630947	0.918158
C	0.817628	2.547260	0.125021
C	2.276018	4.505342	0.530181
H	2.089480	5.477419	0.056091
H	3.357482	4.402636	0.690309
H	1.784003	4.478135	1.502254
C	2.574176	3.106794	-1.489407
H	3.438109	2.459094	-1.272167
H	2.951437	4.044081	-1.908617
H	1.945065	2.629048	-2.245049
C	0.393691	-2.645003	0.147161
C	1.567021	-4.816098	0.333705
H	1.048814	-5.730780	0.648913
H	2.615146	-4.887142	0.653227

H	5.975140	-0.462555	-0.909851	H	1.546705	-4.746918	-0.753755
H	2.192519	-1.329253	0.136331	C	1.189549	-3.410149	2.334919
N	3.083306	1.705085	-0.375913	H	2.151732	-2.910112	2.527905
H	2.139791	2.080294	-0.483578	H	1.204454	-4.379060	2.842437
H	3.689492	2.327151	0.144987	H	0.380197	-2.815987	2.767291
<i>trans-10</i>				<i>cis-10</i>			
Pt	-0.001130	-0.000458	-0.044309	Pt	-0.547252	0.004929	0.293055
Cl	-0.465369	-2.336293	-0.240842	Cl	-2.201055	1.601871	-0.256369
Cl	0.430520	2.343894	0.126890	Cl	-2.108041	-1.742033	-0.020993
N	1.935792	-0.651215	0.119716	N	0.910457	-1.359242	0.787158
C	3.127972	-0.126856	0.068201	H	1.411123	-1.197086	1.654436
C	4.361228	-0.991028	0.194447	N	0.829180	1.504693	0.586172
H	1.945519	-1.662746	0.213791	H	1.329948	1.498020	1.468426
N	3.335387	1.187163	-0.119484	N	0.742923	-2.817914	-1.001374
H	2.537588	1.824448	-0.110727	H	-0.190269	-2.447698	-1.192899
H	4.263516	1.567356	-0.023456	H	0.914391	-3.761329	-1.319272
N	-1.944135	0.622908	-0.220161	N	0.592665	2.680797	-1.392639
C	-3.107809	0.128024	0.090162	H	0.707778	3.579568	-1.839384
C	-4.371582	0.934397	-0.093010	H	-0.315259	2.232045	-1.529261
H	-1.983561	1.590729	-0.525234	C	1.296710	-2.440000	0.170313
N	-3.250780	-1.103491	0.618123	C	2.398928	-3.312107	0.720250
H	-2.451375	-1.736971	0.579846	H	1.981419	-4.254765	1.093214
H	-4.170248	-1.517240	0.646401	H	3.124645	-3.550561	-0.064451
H	4.099336	-2.044798	0.308386	H	2.926297	-2.820259	1.541109
H	4.952016	-0.685582	1.065812	C	1.156276	2.507979	-0.177976
H	4.991578	-0.883065	-0.695115	C	2.198769	3.514707	0.243246
H	-4.153081	1.939227	-0.460093	H	2.752303	3.173738	1.121432
H	-4.906891	1.019544	0.858955	H	1.720549	4.470951	0.486099
H	-5.036540	0.440830	-0.811401	H	2.911552	3.689596	-0.569501
<i>trans-4</i>				<i>cis-4</i>			
Pt	0.764753	-1.020251	0.040850	Pt	-0.548504	0.100992	-0.282939
N	0.977670	-2.232906	1.725093	N	-2.057225	-0.274457	-1.666336
N	0.551885	0.192128	-1.643578	H	-2.571441	0.613435	-1.820881
N	-1.256035	-1.043859	0.391171	H	-2.642955	-1.003409	-1.229964
C	-2.053488	-0.039094	0.652034	H	-1.713908	-0.630667	-2.557487
N	-3.373822	-0.176721	0.968669	N	-2.083931	0.567182	1.042227
C	-3.997663	-1.504361	0.946855	H	-2.655678	-0.288302	1.175997
C	-4.253791	0.989972	0.929788	H	-2.607990	1.329278	0.584562
H	-4.249091	-1.819238	-0.075266	H	-1.754402	0.903316	1.946296
H	-4.912701	-1.462729	1.541488	N	0.897862	-0.120925	-1.726300
H	-3.341062	-2.259839	1.386126	H	1.591819	-0.851591	-1.633493
H	-4.193549	1.522917	-0.027715	N	0.852410	0.238300	1.214737
H	-4.032275	1.695387	1.742005	H	1.592001	0.925872	1.148982
H	-5.280730	0.651778	1.069769	N	0.435788	1.923718	-2.747176
H	-1.615645	-2.004758	0.486931	H	-0.329363	2.106578	-2.076497
N	-1.558753	1.250207	0.548751	H	0.261332	2.330064	-3.656285
H	-2.035957	1.972716	1.069838	N	2.036920	0.510283	-3.686099
H	-0.548241	1.303719	0.638623	N	0.230269	-1.773357	2.215914
N	2.785392	-0.998188	-0.310028	H	-0.517761	-1.911710	1.515913
C	3.581299	-2.004411	-0.570422	H	-0.002806	-2.167232	3.117327
N	4.901703	-1.869248	-0.887624	N	1.875800	-0.456504	3.216390
C	5.528965	-0.543211	-0.866116	C	1.114807	0.749634	-2.697818
C	5.779181	-3.037863	-0.850991	C	2.631367	1.592092	-4.465343
H	4.872326	0.214958	-1.300666	H	2.233039	1.628841	-5.488586
H	6.441031	-0.585859	-1.465265	H	3.715749	1.445099	-4.525803
H	5.786209	-0.231425	0.155522	H	2.449124	2.549767	-3.975362
H	5.555717	-3.741594	-1.664149	C	2.610219	-0.815190	-3.862842
H	5.718361	-3.572044	0.105790	H	3.484719	-0.989943	-3.217150

H	6.806775	-2.701637	-0.990914	H	2.929738	-0.925112	-4.902989
H	3.145975	-0.038012	-0.408802	H	1.859016	-1.583553	-3.660409
N	3.084595	-3.292860	-0.465733	C	0.979574	-0.642028	2.193348
H	2.074073	-3.345410	-0.556300	C	2.374325	-1.570543	4.017175
H	3.561346	-4.016904	-0.985077	H	1.935448	-1.581884	5.024306
H	1.892947	-2.681950	1.774168	H	3.462404	-1.488275	4.119446
H	0.229105	-2.977950	1.682633	H	2.154314	-2.516433	3.519856
H	0.849171	-1.695133	2.582722	C	2.519477	0.832877	3.416345
H	0.677202	-0.346830	-2.500958	H	3.427382	0.954333	2.805481
H	1.302525	0.935303	-1.603969	H	2.804068	0.925343	4.468275
H	-0.362346	0.643439	-1.691460	H	1.823722	1.644141	3.185187
Cl	2.924757	2.085095	-1.095631	Cl	-2.457081	2.807071	-1.412832
Cl	-1.388265	-4.130344	1.163579	Cl	-2.656128	-2.485409	0.770420
<i>trans</i> - 11				<i>cis</i> - 11			
Pt	0.391083	-0.152841	0.060361	Pt	0.296506	0.097399	0.270553
N	0.286654	-0.733744	2.052021	N	-1.395151	1.305929	0.365932
N	0.536775	0.426332	-1.943077	H	-2.095659	0.882770	1.033453
N	2.429559	-0.112267	0.115137	H	-1.806004	1.328565	-0.573075
C	3.342762	-1.048719	0.187701	H	-1.203181	2.262800	0.661112
C	4.810313	-0.686055	0.141757	N	-1.017739	-1.516173	0.294138
H	2.771564	0.842533	0.007765	H	-0.579210	-2.402569	0.542319
N	3.038526	-2.345750	0.297459	H	-1.414589	-1.598942	-0.647515
H	2.087512	-2.702355	0.528255	H	-1.800297	-1.325805	0.977328
H	3.787176	-3.005788	0.451605	N	1.906292	-1.171896	0.139542
N	-1.649285	0.013968	0.004197	H	2.480103	-1.304565	0.964436
C	-2.333632	1.133679	-0.022457	N	1.515535	1.749810	0.213837
C	-3.844942	1.122292	-0.010732	H	2.038983	1.987850	1.048497
H	-2.210125	-0.830616	0.045123	N	1.674134	-1.794189	-2.079170
N	-1.734806	2.329015	-0.063030	H	0.855654	-1.179489	-2.256658
H	-0.709043	2.464027	-0.150933	H	2.017124	-2.334276	-2.859404
H	-2.298695	3.163434	-0.132619	N	1.115992	2.397257	-1.973638
H	4.951827	0.370253	-0.096142	H	1.300379	3.046360	-2.723816
H	5.326777	-1.286928	-0.614316	H	0.485908	1.599258	-2.186797
H	5.279644	-0.890749	1.110759	C	2.310075	-1.852786	-0.905370
H	-4.235036	0.107803	0.096567	C	3.527308	-2.746246	-0.828092
H	-4.235741	1.547976	-0.941690	H	3.277445	-3.761722	-1.153528
H	-4.223076	1.728734	0.819249	H	4.316814	-2.367476	-1.486700
H	1.074557	-0.380226	2.595422	H	3.920921	-2.798670	0.189589
H	0.307910	-1.792665	2.047389	C	1.720638	2.563154	-0.793587
H	-0.571295	-0.423433	2.508247	C	2.661070	3.739852	-0.663689
H	1.227116	-0.125171	-2.452410	H	3.032609	3.843904	0.358312
H	0.856320	1.423146	-1.883956	H	2.151679	4.668826	-0.941282
H	-0.347412	0.374909	-2.448276	H	3.518750	3.614213	-1.333876
Cl	1.347855	3.124249	-0.738368	Cl	-0.832883	0.025734	-2.858854
Cl	0.444670	-3.719203	1.459301	Cl	-3.165475	-0.415406	2.227115