Electronic Supplementary Information

Characterization of a Rhodium-Sparteine Complex, [((—)-sparteine) Rh(η^4-COD)]$^+$: Crystal Structure and DNMR/DFT Studies on Ligand-Rotation Dynamics

Antonio G. De Crisci, Vincent T. Annibale, Gordon K. Hamer, Alan J. Lough, and Ulrich Fekl*

University of Toronto, at the following campus locations: A. G. De C., V. T .A., G. K. H. and U. F. at UTM, Department of Chemical and Physical Sciences, 3359 Mississauga Road N, Mississauga, ON, Canada L5L 1C6; A. J. L. at the X-ray Crystallography Lab, University of Toronto, 80 St. George St., Toronto, ON, Canada M5S 3H6.

* Corresponding author. E-mail: ulrich.fekl@utoronto.ca

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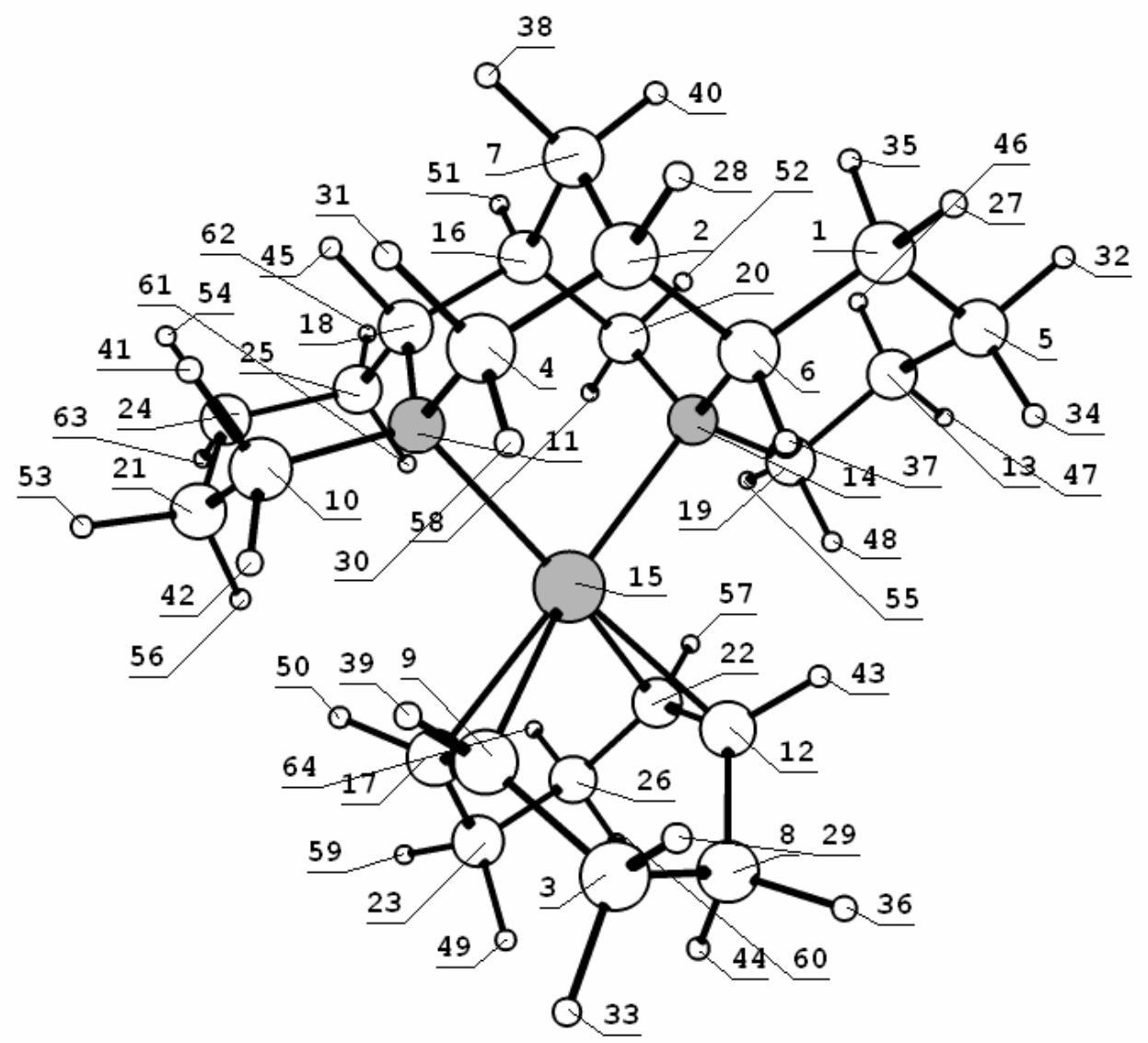
DFT computed atomic coordinates and atom labels for **1**$^{+}$, ground state (singlet) RB3LYP/SDD with augmented d functions on nitrogen [1]



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9	6	0	-2.311349	-0.629171	1.398263
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11	7	0	-0.175833	1.736397	0.650150
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14	7	0	1.576321	-0.484675	-0.530486
15	45	0	-0.658190	-0.392591	-0.020156
16	6	0	2.015982	2.046421	-0.629437
17	6	0	-2.864339	-0.253253	0.149665
18	6	0	0.617237	2.606661	-0.311261
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20	6	0	2.036373	0.692035	-1.355950
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25	6	0	-0.227722	2.970358	-1.546493
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34	1	0	3.314654	-3.153603	0.621002
35	1	0	4.361198	-0.269529	0.578579
36	1	0	-1.550308	-3.985158	1.480319
37	1	0	1.571554	-1.213040	1.440819
38	1	0	2.833907	2.924066	1.190221
39	1	0	-2.184334	0.156635	2.142757
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46	1	0	4.085754	-1.363978	-1.766699
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53	1	0	-2.887328	3.931299	0.457411
54	1	0	-0.944312	4.853012	-0.745642
55	1	0	1.629405	-1.552522	-2.350699
56	1	0	-2.816949	2.453021	-0.488157
57	1	0	-0.484225	-2.096392	-2.087342
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59	1	0	-4.387654	-0.621543	-1.326121
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63	1	0	-2.016179	4.163147	-1.964748

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NROrb= 377 NOA= 103 NOB= 103 NVA= 274 NVB= 274
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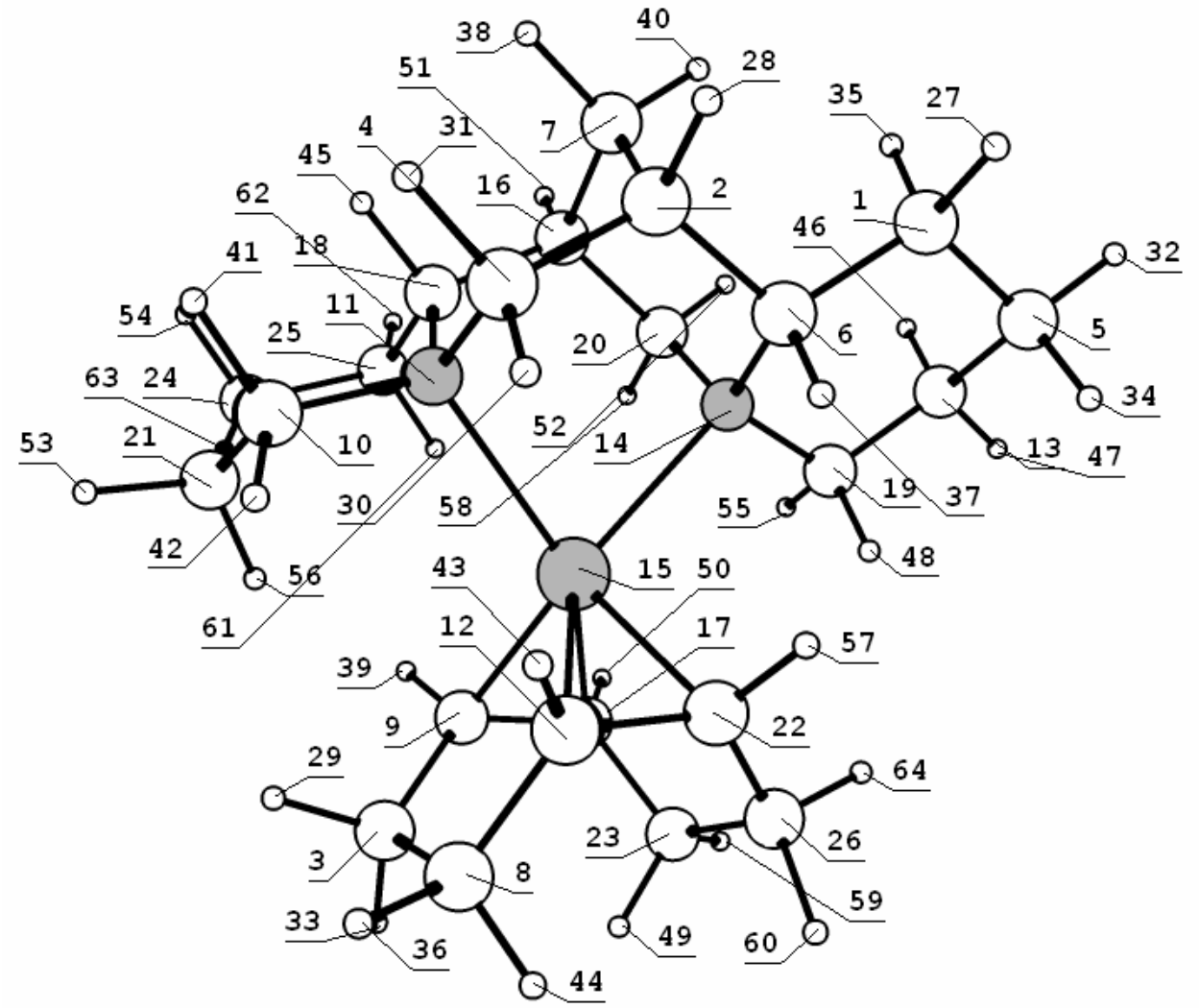
DFT computed atomic coordinates and atom labels for $\mathbf{1_a}^+$, as transition state (singlet) RB3LYP/SDD with augmented d functions on nitrogen[1]



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11	7	0	-0.120196	1.805932	0.655313

12	6	0	-1.636829	-1.184219	1.559065
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14	7	0	1.636457	-0.465797	-0.388265
15	45	0	-0.721637	-0.401006	-0.186464
16	6	0	1.908177	2.061329	-0.834922
17	6	0	-1.982018	-1.628867	-1.369130
18	6	0	0.520911	2.621523	-0.433879
19	6	0	1.924230	-1.809988	-1.011538
20	6	0	1.938413	0.616413	-1.392467
21	6	0	-2.343248	2.928550	0.106830
22	6	0	-0.751188	-2.172482	0.981812
23	6	0	-2.208438	-3.071310	-0.889993
24	6	0	-1.702745	3.601554	-1.125944
25	6	0	-0.471770	2.799006	-1.599115
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28	1	0	2.846995	1.214119	2.360540
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30	1	0	0.372273	0.892965	2.500275
31	1	0	0.919383	2.567171	2.355926
32	1	0	5.144349	-2.369402	0.184194
33	1	0	-4.656889	-1.178901	-0.083773
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35	1	0	4.479187	-0.016072	0.280680
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39	1	0	-2.923986	0.312610	-1.546138
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44	1	0	-3.439562	-2.373491	1.562241
45	1	0	0.718634	3.634167	-0.028686
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47	1	0	3.481365	-3.186635	-1.572948
48	1	0	1.448256	-2.570316	-0.385641
49	1	0	-3.246224	-3.189575	-0.554826
50	1	0	-1.622301	-1.538132	-2.398779
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52	1	0	2.933188	0.454430	-1.832897
53	1	0	-3.087524	3.596112	0.559890
54	1	0	-1.382214	4.622721	-0.872009
55	1	0	1.423941	-1.831146	-1.987876
56	1	0	-2.876081	2.027912	-0.206827
57	1	0	0.224728	-2.275158	1.461922
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Predicted change in Energy=-9.691608D-08
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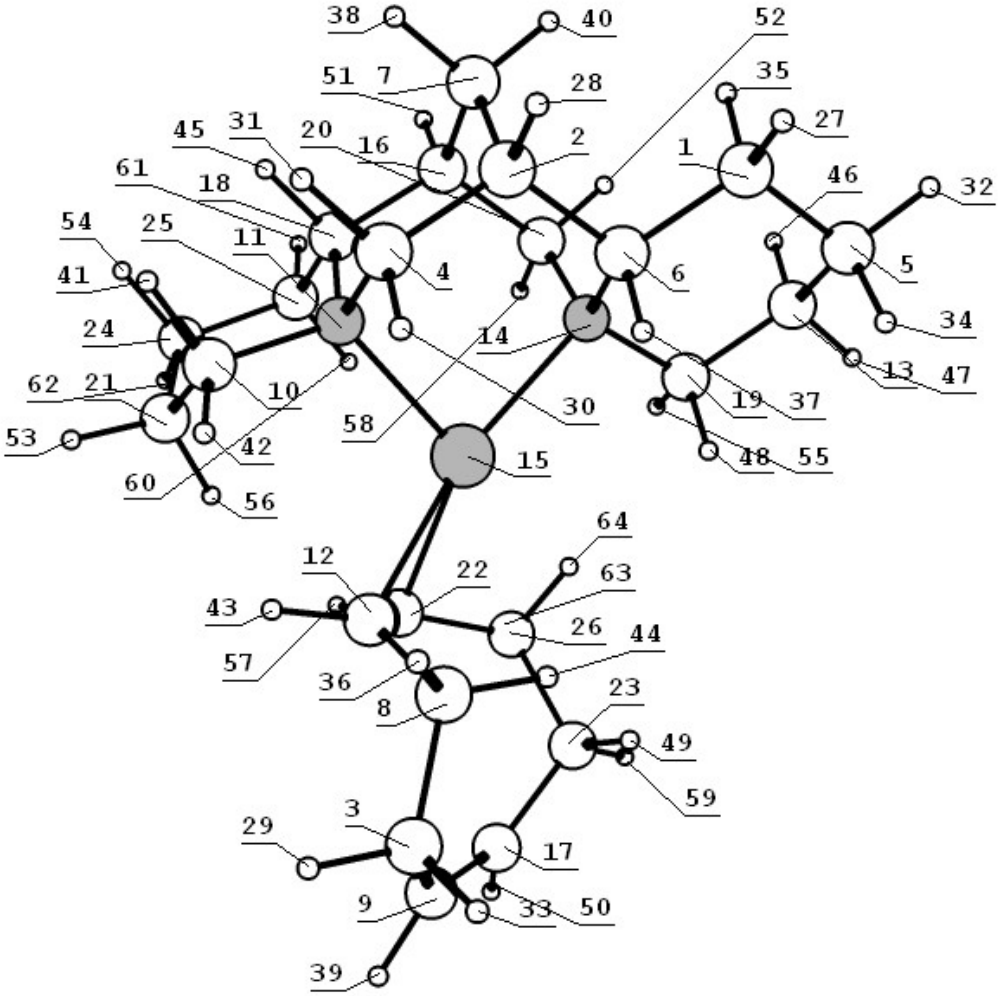

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13	6	0	0.196449	-2.118808	-1.384781

14	7	0	0.955227	-1.855880	1.070620
15	45	0	2.839101	-1.901422	2.165050
16	6	0	-0.516228	-2.272369	3.089595
17	6	0	7.299132	-2.457508	0.784510
18	6	0	0.578655	-2.234950	4.183930
19	6	0	1.293032	-2.336737	-0.323767
20	6	0	-0.059426	-2.768228	1.701448
21	6	0	3.094877	-2.395891	5.676922
22	6	0	4.799235	-2.651841	2.491953
23	6	0	5.949319	-2.605244	0.099799
24	6	0	2.007267	-3.475558	5.866812
25	6	0	1.150733	-3.607139	4.589070
26	6	0	4.798239	-3.107483	1.044229
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28	1	0	-0.342799	1.082810	2.326135
29	1	0	7.335161	0.131581	2.954786
30	1	0	1.977297	0.714023	3.158708
31	1	0	0.724318	0.545820	4.405775
32	1	0	-0.997663	-0.466664	-2.168005
33	1	0	7.311130	0.674861	1.289365
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36	1	0	5.080290	0.798079	2.347158
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44	1	0	5.044743	-0.243018	0.936972
45	1	0	0.082704	-1.814039	5.078097
46	1	0	-0.691249	-2.728926	-1.170032
47	1	0	0.586656	-2.465795	-2.350156
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49	1	0	5.658770	-1.657415	-0.364372
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51	1	0	-1.282487	-2.974685	3.443828
52	1	0	-0.949116	-2.855887	1.061872
53	1	0	3.581589	-2.172654	6.635328
54	1	0	1.358182	-3.204853	6.712889
55	1	0	1.559557	-3.397658	-0.247389
56	1	0	3.869969	-2.773010	5.004367
57	1	0	4.893898	-3.420944	3.253745
58	1	0	0.395823	-3.762369	1.764536
59	1	0	6.039657	-3.329045	-0.719608
60	1	0	1.758841	-4.013404	3.769515
61	1	0	0.316049	-4.299844	4.760659
62	1	0	2.470686	-4.436622	6.119566
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NROrb= 377 NOA= 103 NOB= 103 NVA= 274 NVB= 274
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RMS Displacement	0.000225	0.001200	YES

Predicted change in Energy=-1.299953D-08
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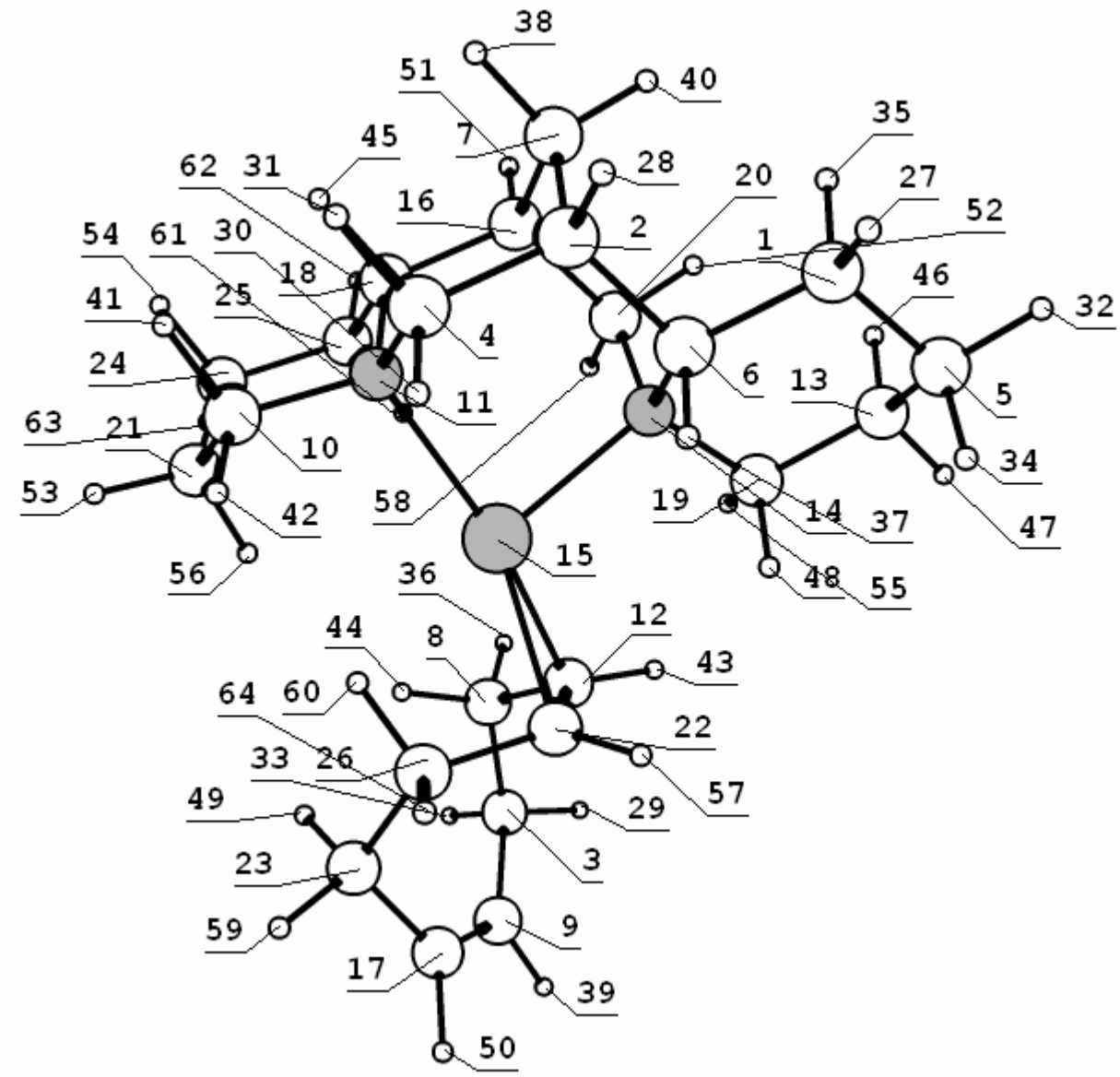
-- Stationary point found.

DFT computed atomic coordinates for $\mathbf{1}_c^+$, as ground state (singlet) RB3LYP/SDD with augmented d functions on nitrogen[1]



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6	6	0	0.553948	-0.082796	1.298075
7	6	0	-0.817940	-1.911328	2.435316

8	6	0	5.822968	-0.426280	3.629139
9	6	0	7.420460	1.679382	3.643546
10	6	0	1.111992	-0.188136	5.830483
11	7	0	1.000666	-0.608355	4.385530
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13	6	0	2.203297	-1.031369	-0.985240
14	7	0	1.853805	-0.853946	1.577470
15	45	0	2.756576	0.034564	3.287797
16	6	0	0.491535	-2.582923	2.895095
17	6	0	6.631991	2.585073	4.267162
18	6	0	0.815367	-2.110607	4.334712
19	6	0	2.800223	-0.724884	0.400834
20	6	0	1.590888	-2.319435	1.840018
21	6	0	2.284306	-0.868421	6.559618
22	6	0	4.241182	1.468376	2.788181
23	6	0	5.361939	2.298989	5.051737
24	6	0	2.189884	-2.405075	6.455849
25	6	0	2.016932	-2.829051	4.982275
26	6	0	4.079165	2.096281	4.164074
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32	1	0	0.542055	-0.336245	-2.221981
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39	1	0	8.312985	2.066009	3.148046
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44	1	0	5.445785	-0.329371	4.652013
45	1	0	-0.078053	-2.342136	4.945001
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54	1	0	1.331020	-2.761413	7.044042
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58	1	0	2.545840	-2.764337	2.135636
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60	1	0	3.381667	1.441129	4.780428
61	1	0	2.934737	-2.597708	4.423402
62	1	0	1.853117	-3.912794	4.913999
63	1	0	3.083921	-2.871541	6.886253

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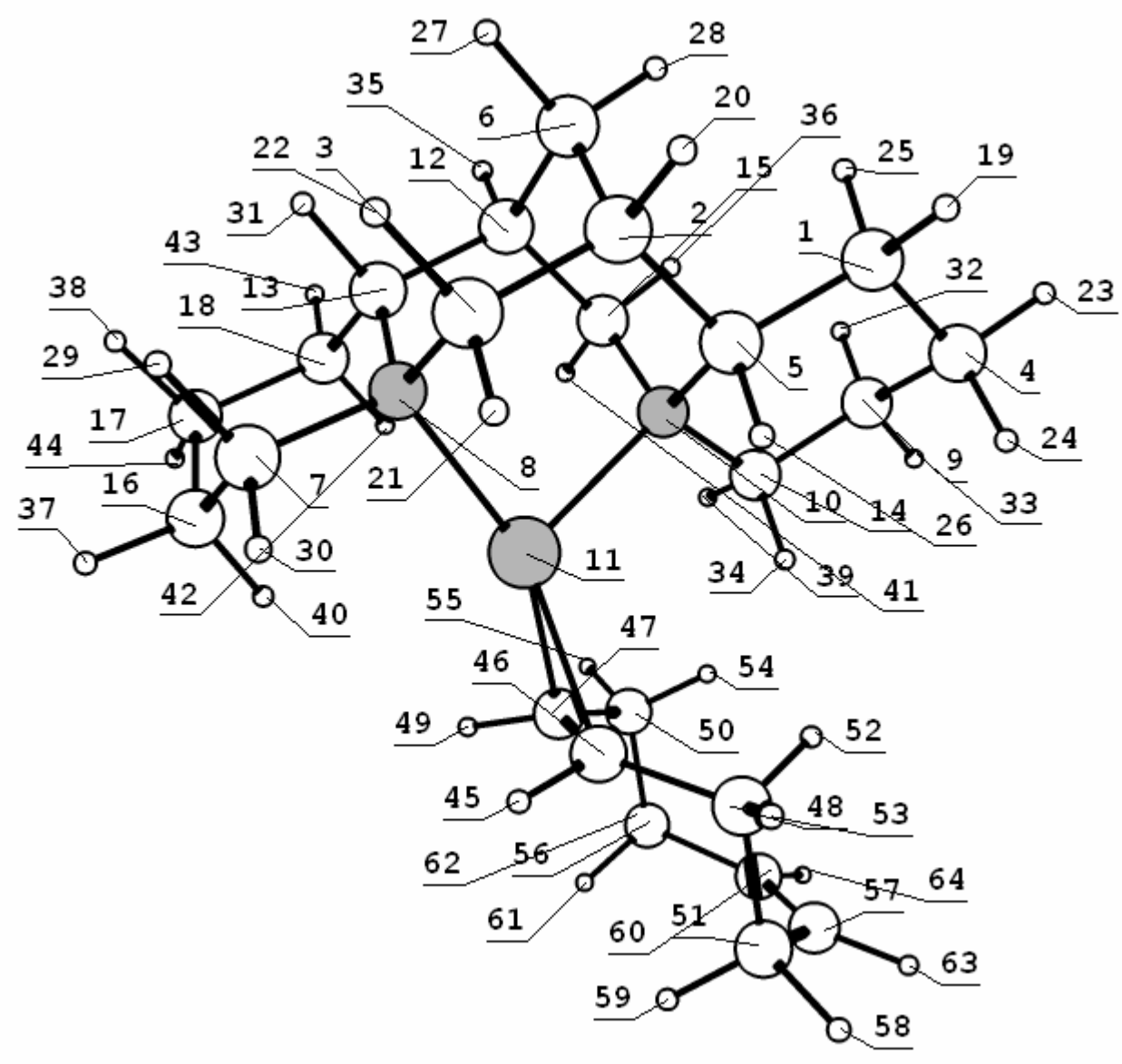
Maximum Displacement         0.001110     0.001800     YES
RMS     Displacement         0.000205     0.001200     YES
Predicted change in Energy=-1.021577D-08
Optimization completed.
  -- Stationary point found.
```

DFT computed atomic coordinates and atomic labels for $\mathbf{1_d}^+$, as ground state (singlet) RB3LYP/SDD with augmented d functions on nitrogen[1]



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.070017	-0.143904	-0.016062
2	6	0	-0.316456	-0.006070	2.523609
3	6	0	0.379031	0.109425	3.894735
4	6	0	0.798408	-0.550344	-1.220338
5	6	0	0.646958	-0.343843	1.349414
6	6	0	-1.440945	-1.059864	2.639460

7	6	0	1.504689	-0.993410	5.754795
8	7	0	0.958406	-1.196081	4.364789
9	6	0	1.258521	-2.007437	-1.040836
10	7	0	1.262007	-1.737782	1.531437
11	45	0	2.636052	-1.666584	3.122619
12	6	0	-0.755186	-2.397520	2.986095
13	6	0	-0.094284	-2.280453	4.382543
14	6	0	2.016039	-2.161946	0.292187
15	6	0	0.207466	-2.781730	1.838977
16	6	0	2.118624	-2.279914	6.335885
17	6	0	1.090371	-3.430012	6.329349
18	6	0	0.493833	-3.603571	4.916802
19	1	0	-0.342755	0.917851	-0.081373
20	1	0	-0.744952	0.979927	2.301255
21	1	0	1.196883	0.838619	3.860868
22	1	0	-0.357640	0.463975	4.635229
23	1	0	0.228365	-0.433624	-2.149555
24	1	0	1.674923	0.110442	-1.298631
25	1	0	-1.008842	-0.709881	-0.051825
26	1	0	1.505427	0.340471	1.378841
27	1	0	-2.145552	-0.772303	3.429859
28	1	0	-2.023327	-1.142303	1.716523
29	1	0	0.685500	-0.647625	6.406862
30	1	0	2.247675	-0.187553	5.706750
31	1	0	-0.884666	-1.955440	5.084623
32	1	0	0.397501	-2.687450	-1.098792
33	1	0	1.944282	-2.304735	-1.844524
34	1	0	2.915224	-1.543870	0.249484
35	1	0	-1.501781	-3.200140	3.051464
36	1	0	-0.397485	-2.949310	0.938022
37	1	0	2.467508	-2.072312	7.355023
38	1	0	0.286212	-3.205756	7.046294
39	1	0	2.325771	-3.198117	0.452884
40	1	0	3.005331	-2.573782	5.752121
41	1	0	0.738784	-3.713612	2.053769
42	1	0	1.277201	-3.965328	4.236222
43	1	0	-0.304624	-4.357246	4.929567
44	1	0	1.559347	-4.363722	6.660882
45	1	0	4.886066	-0.629657	3.523029
46	6	0	4.692945	-1.141268	2.566173
47	6	0	4.637190	-2.553854	2.616944
48	6	0	5.116777	-0.298144	1.372894
49	1	0	4.799298	-3.015795	3.599144
50	6	0	4.986605	-3.497082	1.474808
51	6	0	6.670816	-0.366570	1.143431
52	1	0	4.623198	-0.617240	0.447402
53	1	0	4.820057	0.743233	1.555024
54	1	0	4.531022	-3.187540	0.529620
55	1	0	4.599749	-4.497326	1.711502

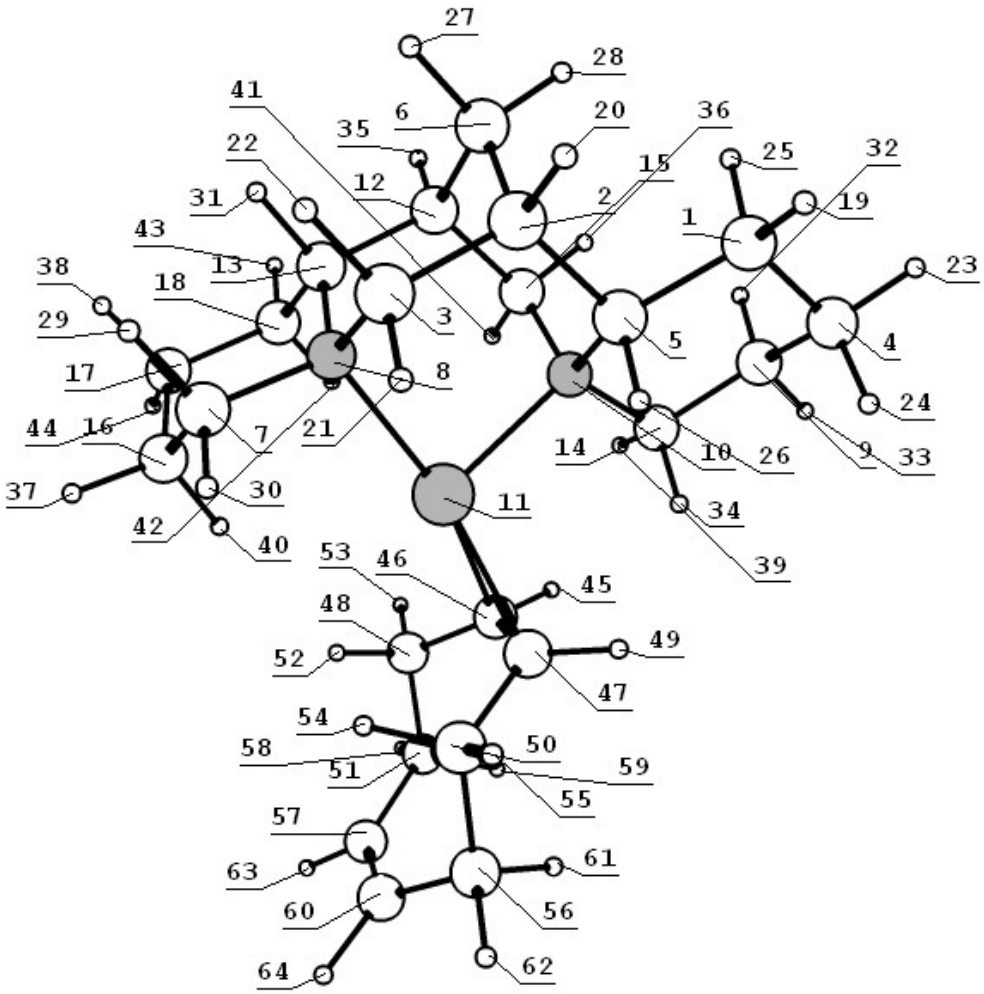
56	6	0	6.542770	-3.576859	1.258162
57	6	0	7.097785	-1.354055	0.064241
58	1	0	7.026729	0.631168	0.860880
59	1	0	7.158469	-0.609875	2.099489
60	6	0	7.046973	-2.706060	0.113721
61	1	0	7.047167	-3.305466	2.197756
62	1	0	6.816812	-4.617692	1.049741
63	1	0	7.484944	-0.904482	-0.851252
64	1	0	7.396271	-3.248388	-0.766114

NBasis= 377 NAE= 103 NBE= 103 NFC= 0 NFV= 0
NROrb= 377 NOA= 103 NOB= 103 NVA= 274 NVB= 274
SCF: E(RB+HF-LYP) = -1119.06904153 a.u.

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.001029	0.001800	YES
RMS Displacement	0.000163	0.001200	YES

Predicted change in Energy=-5.145593D-09
Optimization completed.
-- Stationary point found.

DFT computed atomic coordinates and atomic labels for $\mathbf{1}_e^+$, as ground state (singlet) RB3LYP/SDD with augmented d functions on nitrogen[1]



Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.552984	-0.144991	0.027668
2	6	0	0.394667	0.038739	2.565356
3	6	0	1.117133	-0.009612	3.926800
4	6	0	1.245828	-0.763983	-1.198790
5	6	0	1.220802	-0.535918	1.377345
6	6	0	-0.957449	-0.695609	2.708890
7	6	0	1.931899	-1.329806	5.805313
8	7	0	1.348046	-1.411396	4.418889
9	6	0	1.300086	-2.290808	-1.023970
10	7	0	1.464031	-2.043222	1.550703
11	45	0	2.824433	-2.321233	3.137868
12	6	0	-0.624974	-2.159556	3.061270

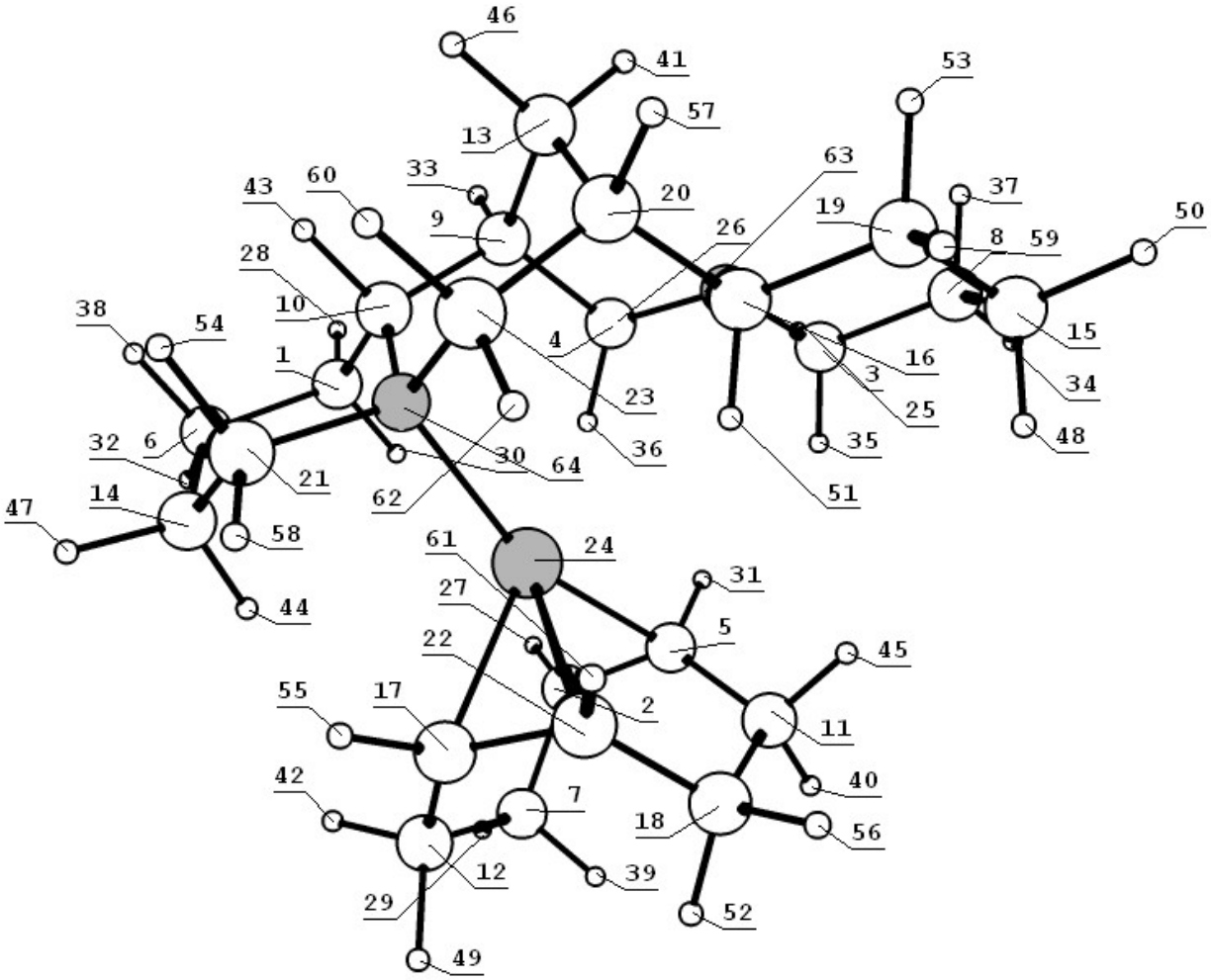
13	6	0	0.058485	-2.197329	4.452691
14	6	0	2.037091	-2.645380	0.281290
15	6	0	0.185825	-2.781620	1.898322
16	6	0	2.208338	-2.720174	6.404292
17	6	0	0.928511	-3.580907	6.411105
18	6	0	0.302764	-3.619421	5.000887
19	1	0	0.576658	0.951286	-0.032571
20	1	0	0.224277	1.099116	2.337544
21	1	0	2.094537	0.484102	3.869315
22	1	0	0.507969	0.537121	4.666611
23	1	0	0.702854	-0.494223	-2.112231
24	1	0	2.265967	-0.364682	-1.304735
25	1	0	-0.504813	-0.434197	0.016318
26	1	0	2.225995	-0.093622	1.389899
27	1	0	-1.554690	-0.233007	3.504555
28	1	0	-1.555493	-0.636394	1.794282
29	1	0	1.227448	-0.782093	6.453429
30	1	0	2.852677	-0.736549	5.745317
31	1	0	-0.623100	-1.680088	5.154063
32	1	0	0.286323	-2.712719	-1.045802
33	1	0	1.850215	-2.762202	-1.848615
34	1	0	3.066020	-2.288010	0.196372
35	1	0	-1.548539	-2.748070	3.144500
36	1	0	-0.467096	-2.797819	1.015092
37	1	0	2.599003	-2.592847	7.421526
38	1	0	0.206315	-3.156880	7.124780
39	1	0	2.064600	-3.728920	0.429956
40	1	0	2.994248	-3.231651	5.827497
41	1	0	0.468351	-3.816577	2.113154
42	1	0	0.969711	-4.170957	4.322715
43	1	0	-0.656913	-4.152469	5.023221
44	1	0	1.153704	-4.597273	6.754823
45	1	0	3.992270	-4.189676	1.427165
46	6	0	4.322654	-3.695512	2.339247
47	6	0	4.782771	-2.356905	2.224239
48	6	0	4.746041	-4.669416	3.436801
49	1	0	4.783362	-1.899482	1.234178
50	6	0	5.736430	-1.684427	3.208075
51	6	0	6.224184	-5.183370	3.255341
52	1	0	4.667690	-4.217932	4.437047
53	1	0	4.057800	-5.524217	3.422692
54	1	0	5.431357	-1.860325	4.252772
55	1	0	5.696897	-0.600306	3.043859
56	6	0	7.223701	-2.182579	3.046644
57	6	0	7.231934	-4.496522	4.164797
58	1	0	6.247041	-6.260507	3.457391
59	1	0	6.511038	-5.056444	2.201036
60	6	0	7.656125	-3.214122	4.077719
61	1	0	7.345156	-2.584366	2.029807
62	1	0	7.888077	-1.313896	3.120490
63	1	0	7.636537	-5.108226	4.971975
64	1	0	8.377354	-2.868740	4.819223

NBasis= 377 NAE= 103 NBE= 103 NFC= 0 NFV= 0
NROrb= 377 NOA= 103 NOB= 103 NVA= 274 NVB= 274
SCF E(RB+HF-LYP) = -1119.07866513

Item	Value	Threshold	Converged?
Maximum Force	0.000024	0.000450	YES
RMS Force	0.000003	0.000300	YES
Maximum Displacement	0.001523	0.001800	YES
RMS Displacement	0.000220	0.001200	YES

Predicted change in Energy=-2.193435D-08
Optimization completed.
-- Stationary point found.

DFT computed atomic coordinates and atomic labels for $\mathbf{1_f}^+$, as ground state (singlet) RB3LYP/SDD with augmented d functions on nitrogen[1]



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.268539	2.590000	-1.488862
2	6	0	-1.815961	-1.901731	-1.457333
3	6	0	3.127977	-0.939173	-1.450795
4	6	0	1.540683	0.917296	-1.461544
5	6	0	-0.505310	-2.307640	-1.127753
6	6	0	-2.598003	3.107088	-0.898123
7	6	0	-3.077556	-2.517372	-0.850955
8	6	0	4.443473	-1.433115	-0.823367
9	6	0	1.271477	2.364469	-0.934850
10	6	0	-0.163023	2.605218	-0.413594
11	6	0	-0.141678	-3.334871	-0.063196
12	6	0	-3.585791	-1.715738	0.378117
13	6	0	2.255934	2.662184	0.215851

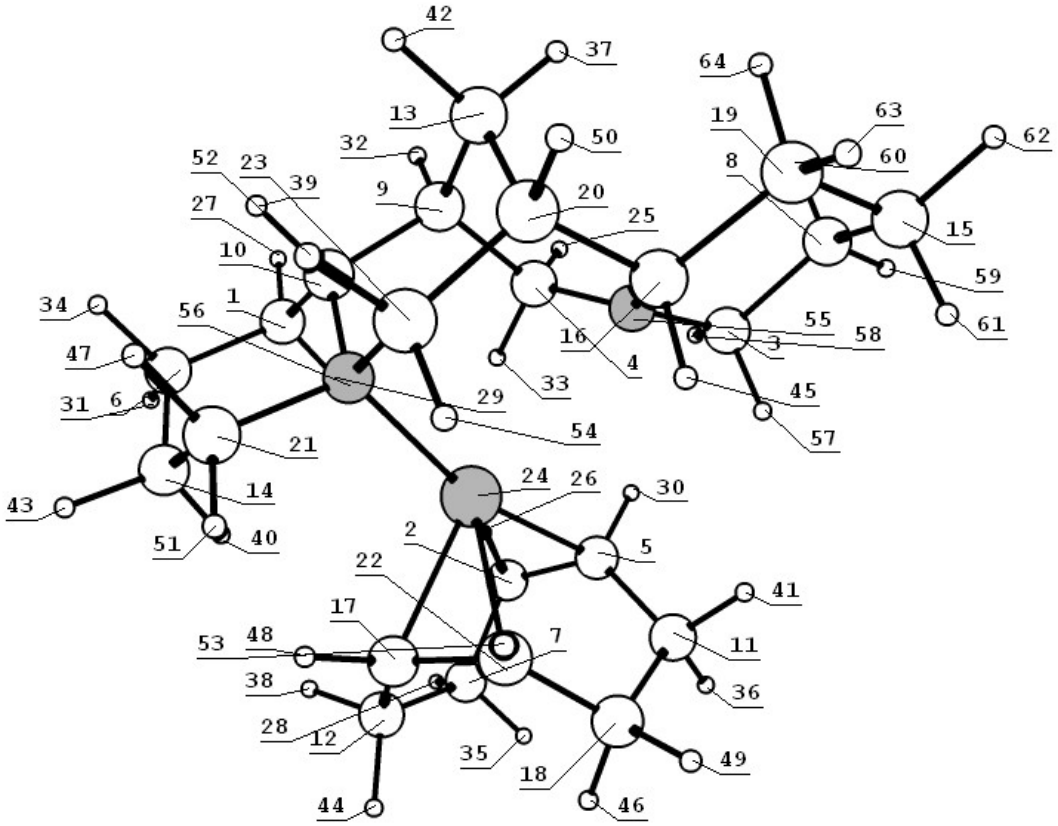
14	6	0	-2.965927	2.313369	0.374709
15	6	0	4.264834	-1.638993	0.694611
16	6	0	2.444616	0.173345	0.656303
17	6	0	-2.462357	-1.023348	1.140369
18	6	0	-0.875574	-3.099407	1.288567
19	6	0	3.727796	-0.347403	1.343223
20	6	0	2.013367	1.556873	1.262488
21	6	0	-1.781631	2.221844	1.356505
22	6	0	-1.224544	-1.625404	1.532339
23	6	0	0.553646	1.648960	1.777858
24	45	0	-0.879017	-0.354000	-0.182124
25	1	0	3.270238	-0.734582	-2.519781
26	1	0	1.692116	0.909764	-2.546836
27	1	0	-1.952033	-1.388652	-2.412030
28	1	0	-0.951101	3.219408	-2.330503
29	1	0	-3.864093	-2.548021	-1.613090
30	1	0	-1.407558	1.572026	-1.891197
31	1	0	0.269867	-2.126863	-1.872191
32	1	0	-3.405383	3.032978	-1.636171
33	1	0	1.428711	3.070930	-1.758841
34	1	0	4.747770	-2.367895	-1.310844
35	1	0	2.368281	-1.740963	-1.362097
36	1	0	0.574684	0.274285	-1.335583
37	1	0	5.233102	-0.692830	-1.009360
38	1	0	-2.488273	4.173931	-0.653534
39	1	0	-2.878592	-3.558215	-0.571867
40	1	0	-0.346397	-4.351919	-0.432798
41	1	0	3.290404	2.643016	-0.134665
42	1	0	-4.291143	-0.945902	0.041699
43	1	0	-0.156674	3.618349	0.026060
44	1	0	-3.287022	1.305104	0.089682
45	1	0	0.940648	-3.279789	0.101575
46	1	0	2.061572	3.656514	0.638771
47	1	0	-3.808801	2.788969	0.892202
48	1	0	3.561147	-2.467694	0.874048
49	1	0	-4.152535	-2.373952	1.056149
50	1	0	5.215770	-1.926677	1.159112
51	1	0	1.625714	-0.566688	0.820676
52	1	0	-1.793240	-3.698275	1.332266
53	1	0	4.497523	0.436371	1.285248
54	1	0	-1.541803	3.229380	1.733230
55	1	0	-2.802261	-0.183781	1.743121
56	1	0	-0.238650	-3.455673	2.106180
57	1	0	2.636965	1.738327	2.147025
58	1	0	-2.033082	1.609240	2.228099
59	1	0	3.514311	-0.511611	2.408436
60	1	0	0.468895	2.589225	2.346579
61	1	0	-0.706258	-1.166920	2.376084
62	1	0	0.334485	0.828989	2.470781
63	7	0	2.656674	0.301089	-0.804484
64	7	0	-0.533672	1.650540	0.719706

NBasis= 377 NAE= 103 NBE= 103 NFC= 0 NFV= 0
NROrb= 377 NOA= 103 NOB= 103 NVA= 274 NVB= 274
SCF: E(RB+HF-LYP) = -1119.08340764 a.u.

Item	Value	Threshold	Converged?
Maximum Force	0.000050	0.000450	YES
RMS Force	0.000004	0.000300	YES
Maximum Displacement	0.001647	0.001800	YES
RMS Displacement	0.000378	0.001200	YES

Predicted change in Energy=-7.890476D-07
Optimization completed.
-- Stationary point found.

DFT computed atomic coordinates and atomic labels for $\mathbf{1_n}^+$, as ground state (singlet) RB3LYP/SDD with augmented d functions on nitrogen[1]



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.152472	2.705017	-1.529917
2	6	0	-1.799630	-1.915213	-1.422090
3	6	0	2.708632	-1.441056	-1.150638
4	6	0	1.435941	0.684364	-1.462406
5	6	0	-0.557422	-2.398543	-0.954443
6	6	0	-2.428444	3.317911	-0.917870
7	6	0	-3.150910	-2.390805	-0.887915
8	6	0	4.246077	-1.472491	-1.027595
9	6	0	1.345749	2.175818	-1.010200
10	6	0	-0.042143	2.587340	-0.466234
11	6	0	-0.370031	-3.392367	0.185269
12	6	0	-3.673463	-1.475551	0.249672
13	6	0	2.388531	2.466182	0.083589
14	6	0	-2.856442	2.505380	0.321753
15	6	0	4.630379	-1.366652	0.460411
16	6	0	2.506681	0.072163	0.838610
17	6	0	-2.547547	-0.818304	1.038800

18	6	0	-1.167649	-3.004972	1.462547
19	6	0	4.043377	-0.073679	1.058536
20	6	0	2.078313	1.504807	1.249345
21	6	0	-1.686464	2.322597	1.306011
22	6	0	-1.395416	-1.491997	1.576775
23	6	0	0.617577	1.682562	1.737210
24	45	0	-0.822824	-0.382144	-0.152077
25	1	0	1.934151	0.642907	-2.442490
26	1	0	-1.817433	-1.457819	-2.413172
27	1	0	-0.779039	3.333741	-2.349111
28	1	0	-3.877904	-2.404699	-1.707504
29	1	0	-1.387352	1.721699	-1.962901
30	1	0	0.289831	-2.316395	-1.632886
31	1	0	-3.238583	3.339081	-1.656219
32	1	0	1.534146	2.804564	-1.888774
33	1	0	0.379416	0.336673	-1.729974
34	1	0	-2.230985	4.361575	-0.631635
35	1	0	-3.061331	-3.425546	-0.537613
36	1	0	-0.644654	-4.406751	-0.143922
37	1	0	3.407268	2.312816	-0.285321
38	1	0	-4.293406	-0.679492	-0.180815
39	1	0	0.084583	3.594644	-0.029781
40	1	0	-3.229937	1.528322	-0.002807
41	1	0	0.697986	-3.428446	0.428710
42	1	0	2.316940	3.514443	0.400609
43	1	0	-3.675384	3.010251	0.850092
44	1	0	-4.330764	-2.040533	0.930361
45	1	0	2.020647	-0.655144	1.516959
46	1	0	-2.137121	-3.517934	1.479591
47	1	0	-1.385736	3.311678	1.689417
48	1	0	-2.866748	0.076222	1.566726
49	1	0	-0.621213	-3.354140	2.345772
50	1	0	2.692196	1.767036	2.121369
51	1	0	-1.981018	1.726365	2.176173
52	1	0	0.566996	2.653229	2.257186
53	1	0	-0.918043	-1.022623	2.439769
54	1	0	0.368050	0.907028	2.470796
55	7	0	2.092414	-0.245796	-0.548879
56	7	0	-0.468556	1.679153	0.678788
57	1	0	2.322033	-2.348644	-0.655804
58	1	0	2.409329	-1.498853	-2.204784
59	1	0	4.625774	-2.405399	-1.465476
60	1	0	4.688396	-0.639168	-1.592836
61	1	0	4.242806	-2.244973	1.000910
62	1	0	5.720006	-1.375428	0.585937
63	1	0	4.233027	-0.037436	2.140639
64	1	0	4.563781	0.785038	0.611569

NBasis= 377 NAE= 103 NBE= 103 NFC= 0 NFV= 0
NROrb= 377 NOA= 103 NOB= 103 NVA= 274 NVB= 274
SCF E(RB+HF-LYP) = -1119.06643025
****** 1 imaginary frequencies (negative Signs) ******
Frequencies -- -317.8203

Item	Value	Threshold	Converged?
Maximum Force	0.000010	0.000450	YES
RMS Force	0.000001	0.000300	YES
Maximum Displacement	0.000613	0.001800	YES
RMS Displacement	0.000082	0.001200	YES

Predicted change in Energy=-6.098708D-09
Optimization completed.
-- Stationary point found.

Molecular Orbitals

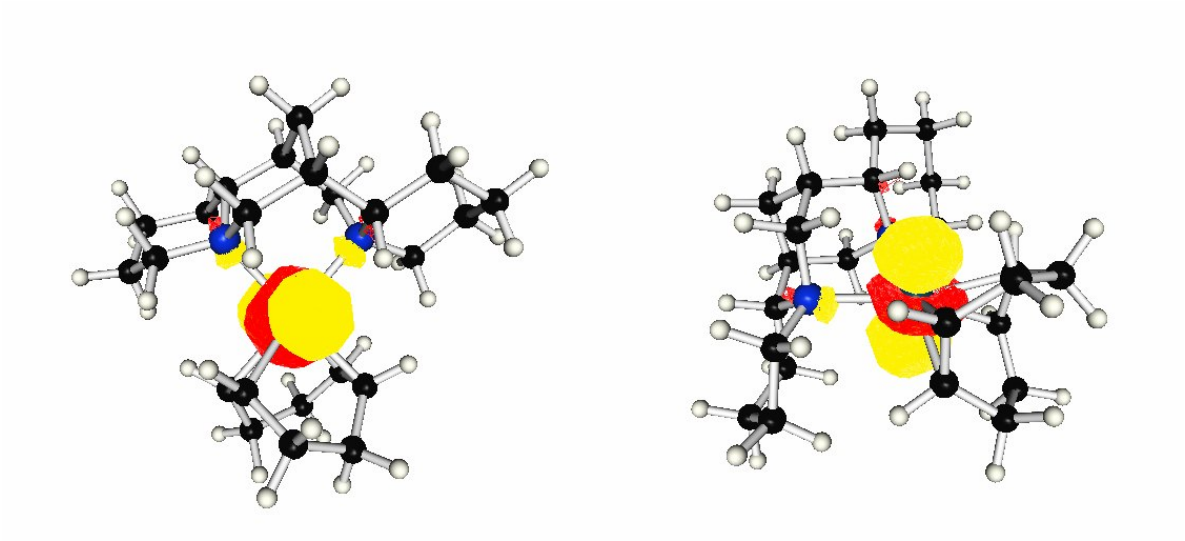


Figure S1: Highest Occupied Molecular Orbital (HOMO) of $\mathbf{1}^{+}$ calculated at RB3LYP/SDD with isovalue of 0.04[2]. View #1 (left) and View #2 (right).

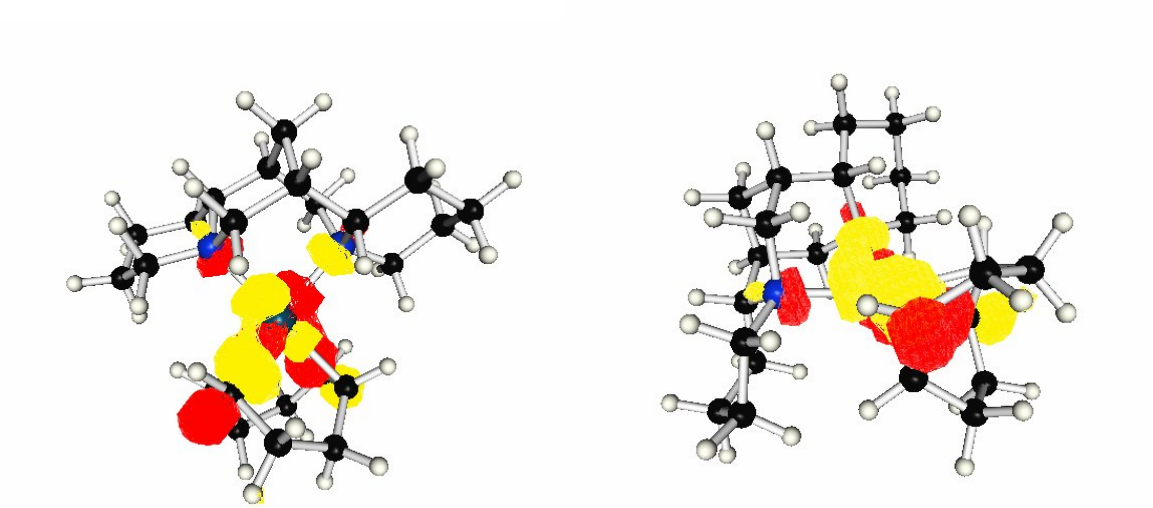


Figure S2: Lowest Unoccupied Molecular Orbital (LUMO) of $\mathbf{1}^{+}$ calculated at RB3LYP/SDD with isovalue of 0.04.[2] View #1 (left) and View #2 (right).

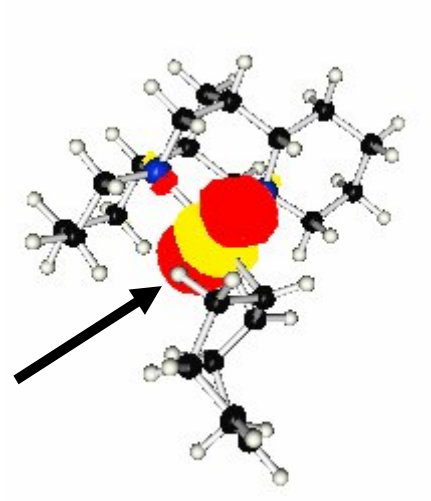


Figure S3: Highest Occupied Molecular Orbital (HOMO) of $\mathbf{1_c}^+$ calculated at RB3LYP/SDD with isovalue of 0.04.[2] Arrow pointing to H60 (agostic proton), revealing a 1.14 Å C-H bond.

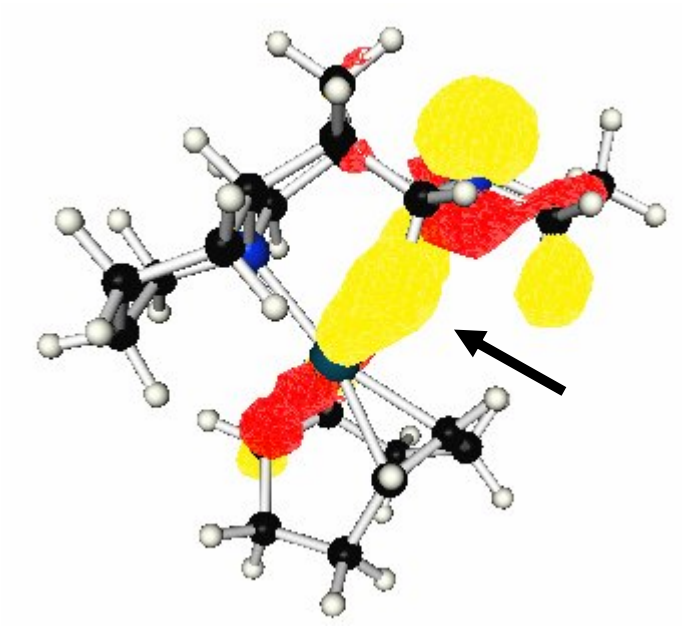


Figure S4: Highest Occupied Molecular Orbital (HOMO) of $\mathbf{1_f}^+$ calculated at RB3LYP/SDD with isovalue of 0.04.[2] Arrow pointing to Rh-H46 agostic interaction, revealing a 1.17 Å C-H bond and a Rh-H46 bond length of 1.96 Å for the pseudo square planar metal center.

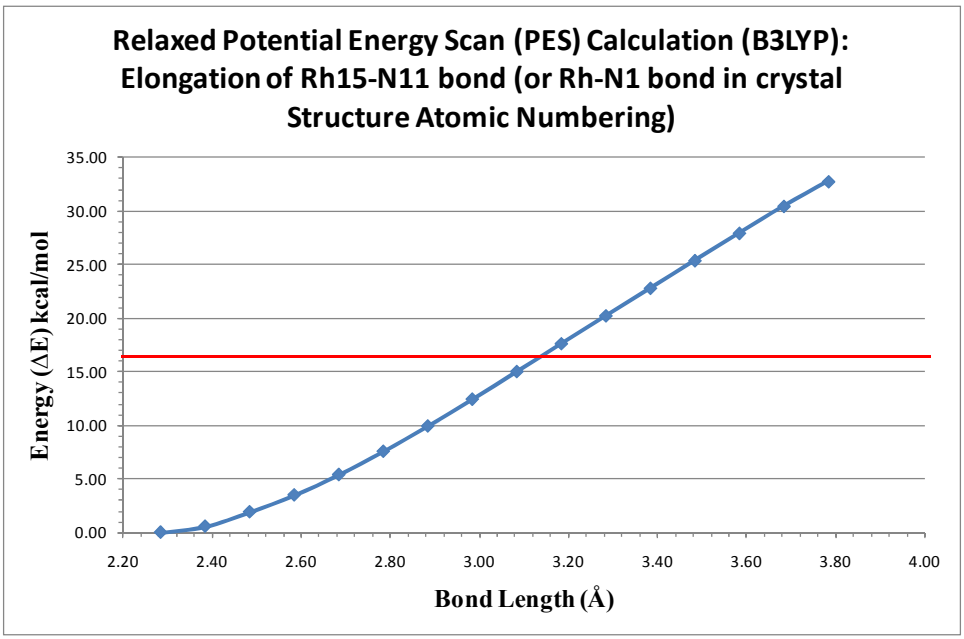


Figure S5: Relaxed Potential Energy Scan (PES) calculation. Plot correlates the energy of the molecule with respect to to the elongation of the Rh15-N11 bond (or Rh-N1 bond in crystal structure atomic numbering). At a Rh-N bond length of 3.18 Å (0.9 Å larger than the ground state value) the energy of the $\mathbf{1}^+$, approaches the energy of complex, $\mathbf{1_a}^+$ (denoted by the red, horizontal line in the plot). Starting Rh-N bond length, 2.28354 Å. Final Rh-N bond length: 3.78354 Å. Final structure shown below in Figure S6.

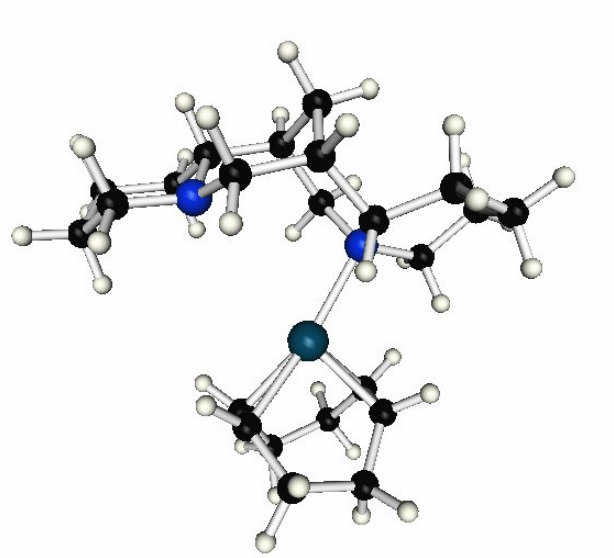


Figure S6: Geometry optimized structure from the final coordinates of the PES scan (B3LYP) showing the elongated Rh-N at 3.78 Å (or 1.5 Å longer than the ground state molecule, $\mathbf{1}^+$). At this distance, the energy of the molecule is 32.78 kcal/mol (ΔE) higher than the ground state energy.

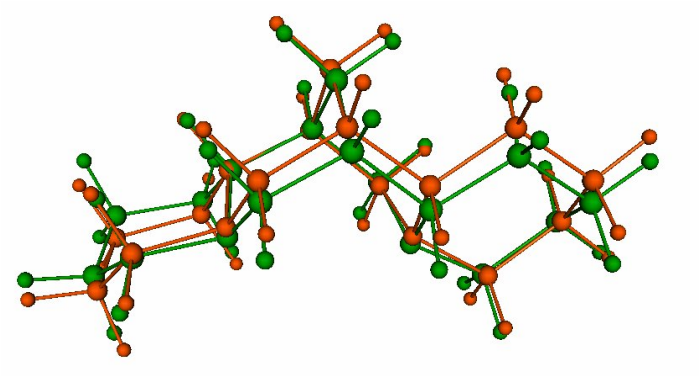


Figure S7: Geometry of (-)sparteine from $\mathbf{1}^+$ (green) and $\mathbf{1_a}^+$ (orange) showing the flexing of the (-)sparteine at the transition state where rhodium (not shown) is defined as the 0,0,0 point of the Cartesian coordinates.[3]

Table S1: DFT computed Energies for CPCM computed molecules of complexes in a.u. units calculated at B3LYP/SDD (energies for non-CPCM molecules on Pages S3 to 26 below atomic coordinates).

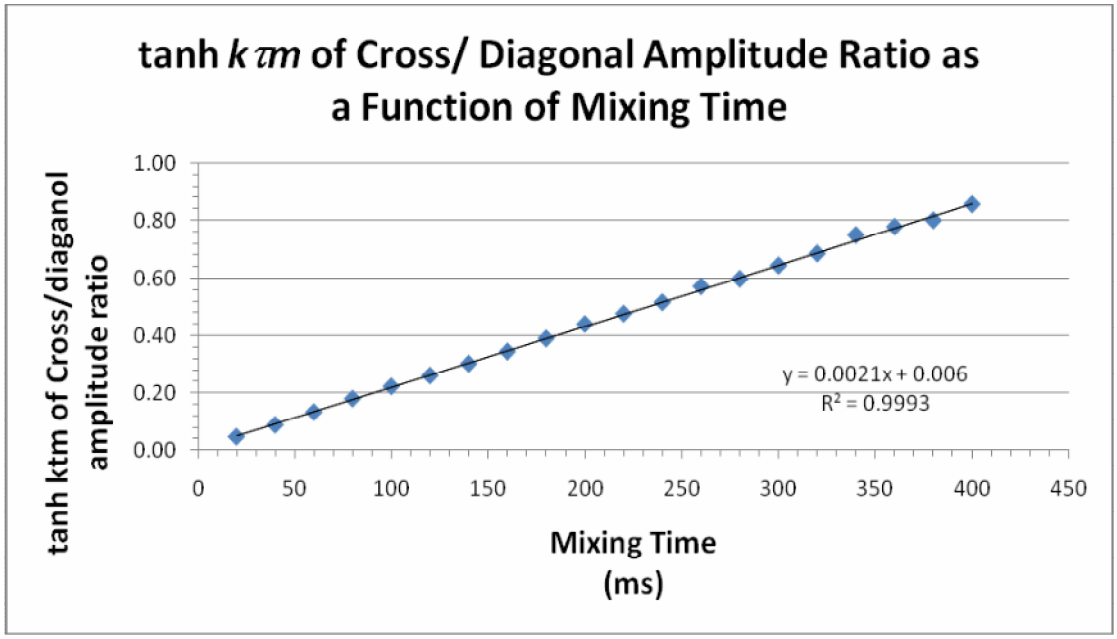
Compound	SCF Energy with CPCM Solvent model of Select Compounds (dichloromethane, UFF)
$\mathbf{1}^+$	-1119.15924504
$\mathbf{1_a}^+$	-1119.13231009
$\mathbf{1_c}^+$	-1119.13069812
$\mathbf{1_f}^+$	-1119.13461581
$\mathbf{1_n}^+$	-1119.11727193

Table S2: Tabulated thermodynamic values (DFT) of complexes in a.u. units calculated at B3LYP/SDD from vibrational analysis at 298.15 K in gas phase.

Compound	Sum of electronic and thermal Free Energies; $G_{298.15}$ (a.u.)	Sum of electronic and thermal Enthalpies; $H_{298.15}$ (a.u.)
$\mathbf{1}^+$	-1118.566161	-1118.493462
$\mathbf{1_a}^+$	-1118.541382	-1118.469949
$\mathbf{1_b}^+$	-1118.539056	-1118.464229
$\mathbf{1_c}^+$	-1118.541246	-1118.465359
$\mathbf{1_d}^+$	-1118.533126	-1118.456044
$\mathbf{1_e}^+$	-1118.542239	-1118.465715
$\mathbf{1_f}^+$	-1118.546655	-1118.472336
$\mathbf{1_n}^+$	-1118.529084	-1118.455394
With CPCM Solvent model of Select Compounds (dichloromethane, UFF)		
$\mathbf{1}^+$	-1118.617615	-1118.545432
$\mathbf{1_a}^+$	-1118.592620	-1118.521487
$\mathbf{1_c}^+$	-1118.594288	-1118.518421
$\mathbf{1_f}^+$	-1118.598534	-1118.524437
$\mathbf{1_n}^+$	-1118.581381	-1118.507376

Table S3: EXSY data taken at -20 °C in CD_2Cl_2.

t (ms)	c/d ratio	tanh-1 (c/d)	k (sec-1)
20	0.0463	0.0463	2.317
40	0.0877	0.0879	2.198
60	0.1316	0.1324	2.206
80	0.1774	0.1793	2.241
100	0.2185	0.2221	2.221
120	0.2545	0.2602	2.168
140	0.2926	0.3014	2.153
160	0.3310	0.3440	2.150
180	0.3709	0.3895	2.164
200	0.4136	0.4399	2.200
220	0.4436	0.4767	2.167
240	0.4750	0.5165	2.152
260	0.5168	0.5720	2.200
280	0.5355	0.5978	2.135
300	0.5674	0.6437	2.146
320	0.5947	0.6849	2.140
340	0.6342	0.7484	2.201
360	0.6510	0.7770	2.158
380	0.6638	0.7996	2.104
400	0.6939	0.8554	2.139



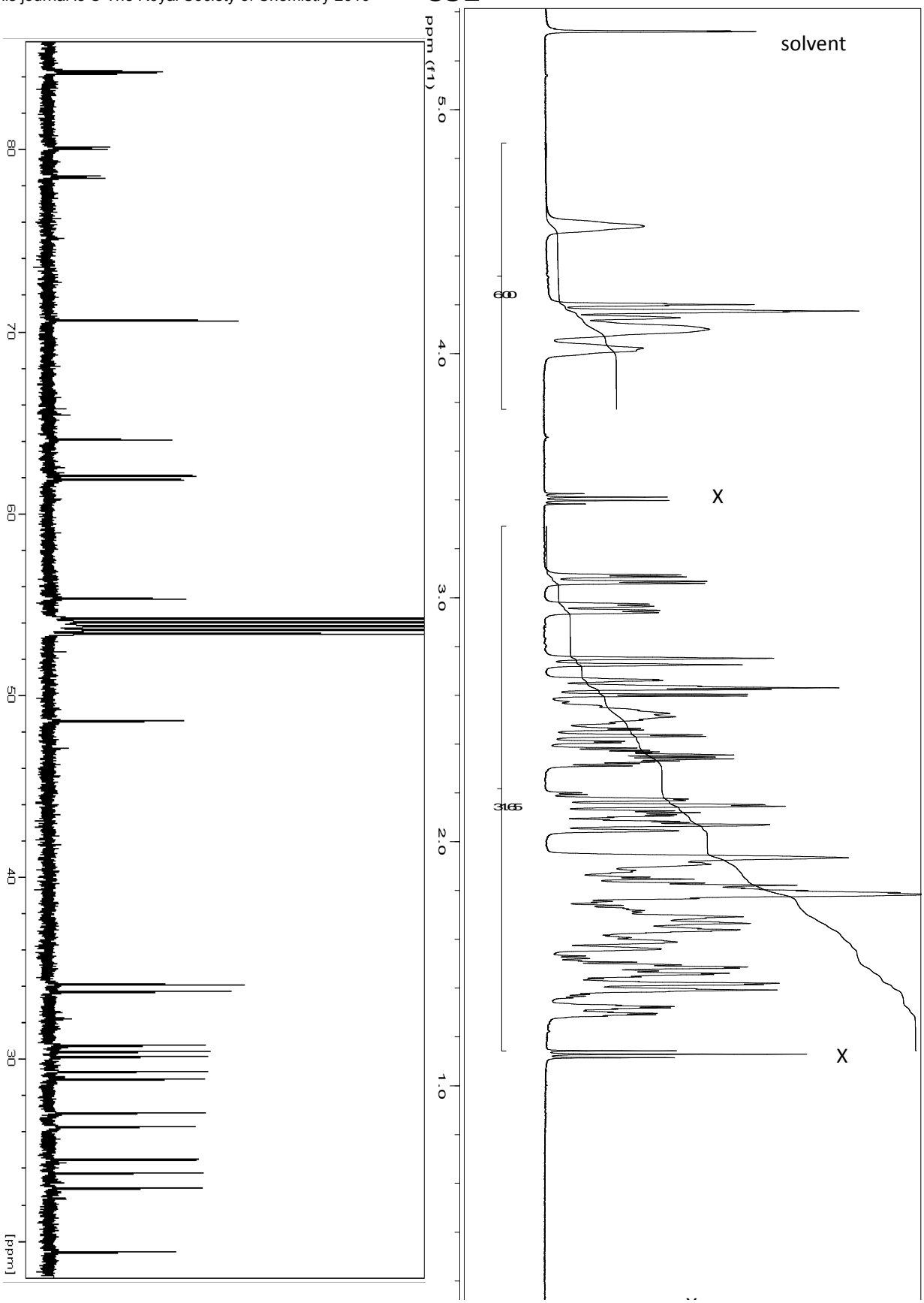


Figure S8: ^{1}H (500 MHz; -10 ^{o}C) and ^{13}C NMR (125 MHz; -40 ^{o}C) of **1**BF_4 in CD_2Cl_2. 'x' denotes ether peaks.

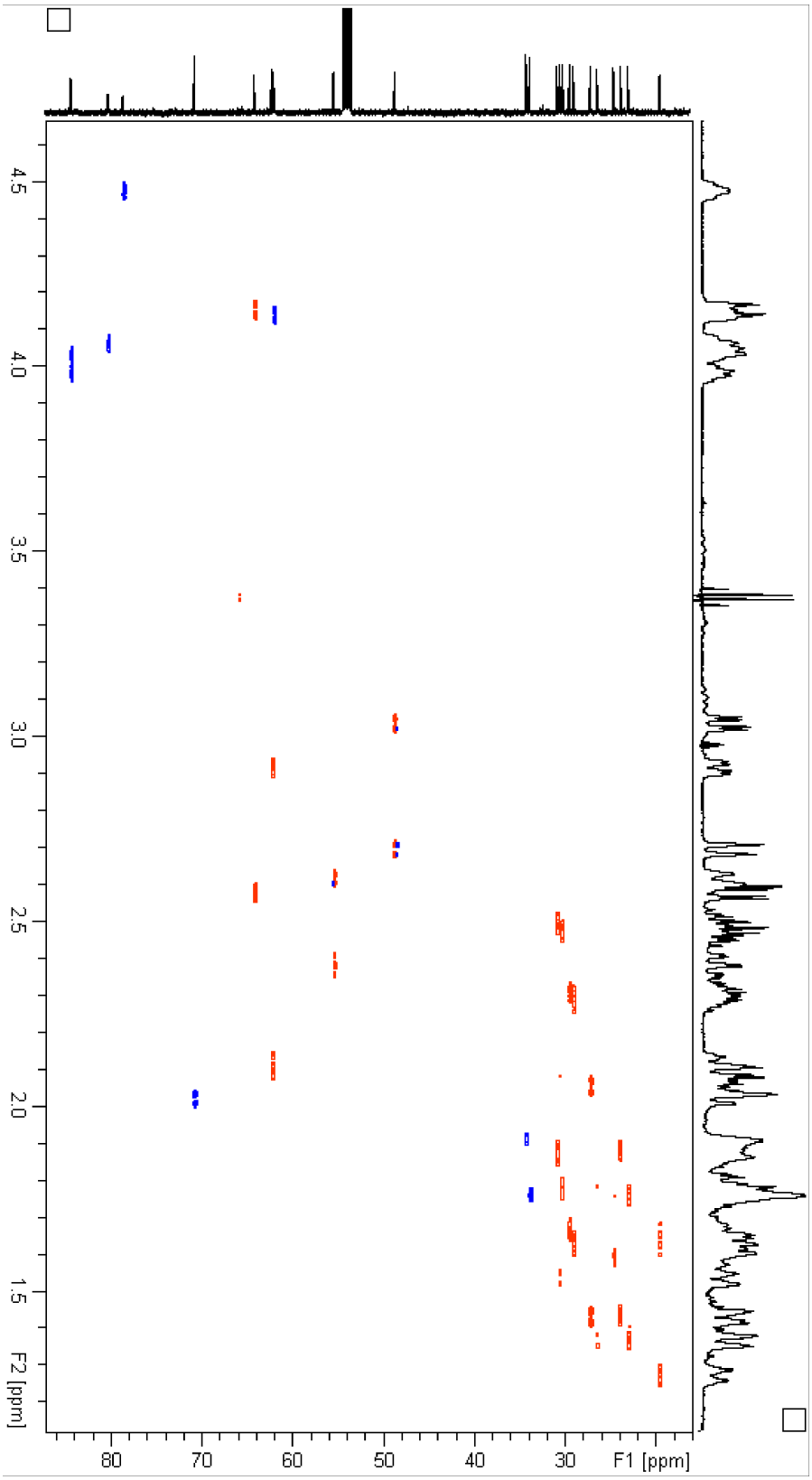


Figure S9: Phase sensitive gHSQC of **1**BF_4 in CD_2Cl_2 at -50 ^oC. Blue is positive, red is negative.

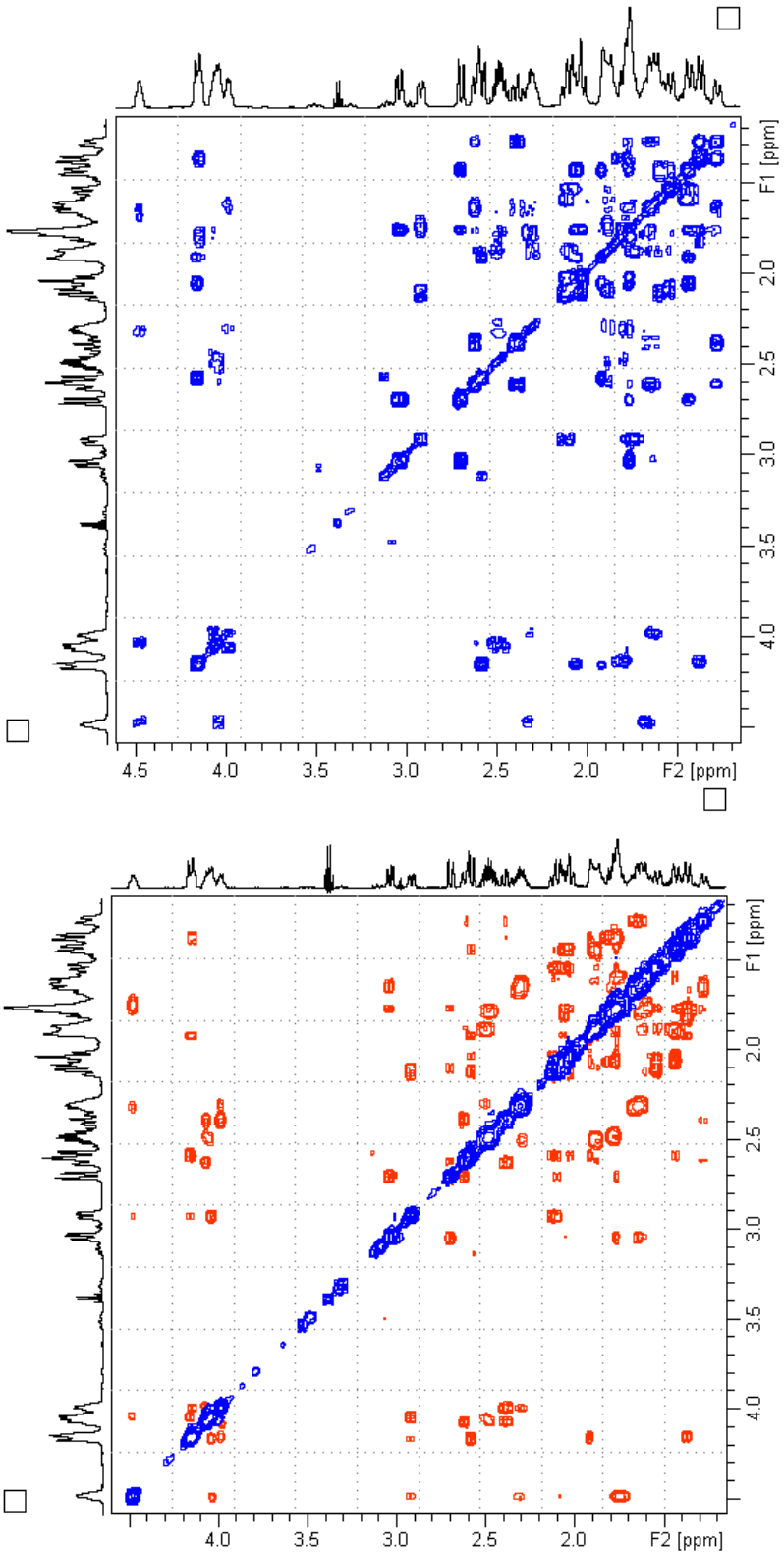


Figure S10: gCOSY (top) and phase sensitive NOESY (bottom) of **1**BF_4 in CD_2Cl_2, at-50 ^oC. Blue is positive, red is negative.

Detailed Crystal Structure Information

Table S4. Crystal data and structure refinement for k08228 (CCDC 730 876).

Identification code	k08228 (CCDC 730 876)	
Empirical formula	C23 H38 B F4 N2 Rh	
Formula weight	532.27	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C 2 2 21	
Unit cell dimensions	a = 14.1899(3) Å	α= 90°.
	b = 14.3150(3) Å	β= 90°.
	c = 23.4356(5) Å	γ = 90°.
Volume	4760.44(17) $Å^3$	
Z	8	
Density (calculated)	1.485 Mg/m^3	
Absorption coefficient	0.761 mm^{-1}	
F(000)	2208	
Crystal size	0.22 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.67 to 27.48°.	
Index ranges	-18<=h<=18, -18<=k<=18, -30<=l<=30	
Reflections collected	16475	
Independent reflections	5411 [R(int) = 0.054]	
Completeness to theta = 27.48°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.922 and 0.852	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5411 / 4 / 292	
Goodness-of-fit on F^2	1.086	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.0922	
R indices (all data)	R1 = 0.0533, wR2 = 0.0987	
Absolute structure parameter	-0.02(3)	
Largest diff. peak and hole	1.217 and -0.724 $e.Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for k08228 (CCDC 730 876). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	3138(1)	6432(1)	6347(1)	19(1)
N(1)	1814(2)	6351(2)	5850(1)	20(1)
N(16)	2245(2)	5931(2)	7074(2)	22(1)
C(2)	1835(3)	6704(3)	5245(2)	27(1)
C(3)	1802(4)	7765(3)	5199(2)	36(1)
C(4)	953(4)	8180(3)	5515(2)	38(1)
C(5)	960(3)	7809(3)	6120(2)	33(1)
C(6)	901(3)	6745(3)	6096(2)	26(1)
C(7)	631(3)	6304(3)	6653(2)	29(1)
C(8)	466(3)	5258(3)	6568(2)	29(1)
C(9)	1434(3)	4852(3)	6390(2)	24(1)
C(10)	1721(3)	5299(3)	5827(2)	25(1)
C(11)	2133(3)	4929(3)	6887(2)	24(1)
C(12)	1839(3)	4240(3)	7360(2)	34(1)
C(13)	2422(3)	4361(4)	7907(2)	43(1)
C(14)	2327(3)	5347(4)	8109(2)	37(1)
C(15)	2709(3)	6001(3)	7654(2)	29(1)
C(17)	1328(3)	6435(3)	7144(2)	26(1)
C(18)	4011(3)	6133(3)	5620(2)	26(1)
C(19)	4007(3)	7085(3)	5703(2)	29(1)
C(20)	4823(3)	7636(3)	5949(2)	36(1)
C(21)	4756(3)	7752(3)	6596(2)	36(1)
C(22)	4247(3)	6951(3)	6875(2)	28(1)
C(23)	4430(3)	6016(3)	6759(2)	27(1)
C(24)	5200(3)	5673(3)	6358(2)	31(1)
C(25)	4785(3)	5470(3)	5769(2)	30(1)
F(1)	3644(2)	7977(2)	4078(2)	62(1)
F(2)	3588(2)	7096(2)	3271(1)	52(1)
F(3)	2236(2)	7439(2)	3739(1)	46(1)
F(4)	3293(2)	6435(2)	4130(1)	46(1)
B(1)	3187(4)	7252(3)	3801(2)	31(1)

Table S6. Bond lengths [Å] and angles [°] for k08228 (CCDC 730 876).

Rh(1)-C(22)	2.134(4)
Rh(1)-C(18)	2.149(4)
Rh(1)-C(23)	2.155(4)
Rh(1)-C(19)	2.161(4)
Rh(1)-N(1)	2.214(3)
Rh(1)-N(16)	2.242(3)
N(1)-C(2)	1.506(5)
N(1)-C(10)	1.513(5)
N(1)-C(6)	1.527(5)
N(16)-C(17)	1.496(5)
N(16)-C(11)	1.508(5)
N(16)-C(15)	1.513(5)
C(2)-C(3)	1.523(6)
C(3)-C(4)	1.535(6)
C(4)-C(5)	1.514(7)
C(5)-C(6)	1.525(6)
C(6)-C(7)	1.498(6)
C(7)-C(17)	1.529(6)
C(7)-C(8)	1.530(6)
C(8)-C(9)	1.548(6)
C(9)-C(10)	1.520(6)
C(9)-C(11)	1.535(6)
C(11)-C(12)	1.540(6)
C(12)-C(13)	1.536(7)
C(13)-C(14)	1.495(7)
C(14)-C(15)	1.518(6)
C(18)-C(19)	1.377(6)
C(18)-C(25)	1.493(6)
C(19)-C(20)	1.515(7)
C(20)-C(21)	1.527(7)
C(21)-C(22)	1.505(6)
C(22)-C(23)	1.390(6)

C(23)-C(24)	1.523(6)
C(24)-C(25)	1.530(6)
F(1)-B(1)	1.385(6)
F(2)-B(1)	1.384(6)
F(3)-B(1)	1.383(6)
F(4)-B(1)	1.409(5)

C(22)-Rh(1)-C(18)	95.96(17)
C(22)-Rh(1)-C(23)	37.83(17)
C(18)-Rh(1)-C(23)	79.06(18)
C(22)-Rh(1)-C(19)	80.42(18)
C(18)-Rh(1)-C(19)	37.26(17)
C(23)-Rh(1)-C(19)	87.00(16)
C(22)-Rh(1)-N(1)	161.56(15)
C(18)-Rh(1)-N(1)	93.52(15)
C(23)-Rh(1)-N(1)	160.53(14)
C(19)-Rh(1)-N(1)	98.00(15)
C(22)-Rh(1)-N(16)	95.05(15)
C(18)-Rh(1)-N(16)	149.83(15)
C(23)-Rh(1)-N(16)	92.97(15)
C(19)-Rh(1)-N(16)	172.64(15)
N(1)-Rh(1)-N(16)	84.44(12)
C(2)-N(1)-C(10)	107.6(3)
C(2)-N(1)-C(6)	104.4(3)
C(10)-N(1)-C(6)	107.9(3)
C(2)-N(1)-Rh(1)	117.5(2)
C(10)-N(1)-Rh(1)	98.3(2)
C(6)-N(1)-Rh(1)	120.1(2)
C(17)-N(16)-C(11)	113.5(3)
C(17)-N(16)-C(15)	104.4(3)
C(11)-N(16)-C(15)	111.6(3)
C(17)-N(16)-Rh(1)	114.9(2)
C(11)-N(16)-Rh(1)	98.2(2)
C(15)-N(16)-Rh(1)	114.6(2)
N(1)-C(2)-C(3)	113.6(3)
C(2)-C(3)-C(4)	112.1(4)

C(5)-C(4)-C(3)	108.1(4)
C(4)-C(5)-C(6)	108.4(4)
C(7)-C(6)-C(5)	113.8(4)
C(7)-C(6)-N(1)	112.9(3)
C(5)-C(6)-N(1)	109.7(3)
C(6)-C(7)-C(17)	116.0(3)
C(6)-C(7)-C(8)	109.8(4)
C(17)-C(7)-C(8)	108.5(4)
C(7)-C(8)-C(9)	105.5(3)
C(10)-C(9)-C(11)	117.1(3)
C(10)-C(9)-C(8)	108.3(3)
C(11)-C(9)-C(8)	110.0(4)
N(1)-C(10)-C(9)	114.3(3)
N(16)-C(11)-C(9)	110.9(3)
N(16)-C(11)-C(12)	115.4(4)
C(9)-C(11)-C(12)	109.0(3)
C(13)-C(12)-C(11)	112.5(4)
C(14)-C(13)-C(12)	108.8(4)
C(13)-C(14)-C(15)	109.1(4)
N(16)-C(15)-C(14)	115.8(3)
N(16)-C(17)-C(7)	114.9(3)
C(19)-C(18)-C(25)	126.8(4)
C(19)-C(18)-Rh(1)	71.8(3)
C(25)-C(18)-Rh(1)	111.5(3)
C(18)-C(19)-C(20)	124.4(5)
C(18)-C(19)-Rh(1)	70.9(3)
C(20)-C(19)-Rh(1)	113.3(3)
C(19)-C(20)-C(21)	112.7(4)
C(22)-C(21)-C(20)	112.2(4)
C(23)-C(22)-C(21)	124.1(4)
C(23)-C(22)-Rh(1)	71.9(3)
C(21)-C(22)-Rh(1)	111.6(3)
C(22)-C(23)-C(24)	124.4(4)
C(22)-C(23)-Rh(1)	70.3(3)
C(24)-C(23)-Rh(1)	115.0(3)
C(23)-C(24)-C(25)	110.0(3)

C(18)-C(25)-C(24)	111.9(4)
F(3)-B(1)-F(2)	109.8(4)
F(3)-B(1)-F(1)	111.2(4)
F(2)-B(1)-F(1)	110.4(4)
F(3)-B(1)-F(4)	108.8(4)
F(2)-B(1)-F(4)	108.2(4)
F(1)-B(1)-F(4)	108.4(4)

Symmetry transformations used to generate equivalent atoms:

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for k08228 (CCDC 730 876). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	16(1)	20(1)	22(1)	-1(1)	1(1)	-1(1)
N(1)	17(1)	22(2)	20(2)	-2(1)	1(1)	6(2)
N(16)	16(2)	29(2)	21(2)	0(2)	-1(1)	-3(1)
C(2)	28(2)	31(2)	21(2)	-3(2)	-5(2)	8(2)
C(3)	42(3)	35(2)	31(2)	10(2)	2(2)	9(2)
C(4)	40(3)	35(2)	39(3)	2(2)	3(2)	20(2)
C(5)	37(2)	27(2)	35(3)	-6(2)	3(2)	14(2)
C(6)	18(2)	27(2)	32(2)	-7(2)	-1(2)	5(2)
C(7)	17(2)	32(2)	39(2)	-8(2)	3(2)	0(2)
C(8)	16(2)	32(2)	38(3)	-2(2)	-2(2)	-5(2)
C(9)	23(2)	21(2)	30(2)	0(2)	2(2)	-2(2)
C(10)	22(2)	25(2)	27(2)	-6(2)	-1(2)	-3(2)
C(11)	21(2)	20(2)	31(2)	0(2)	2(2)	1(2)
C(12)	32(2)	30(2)	41(3)	13(2)	3(2)	4(2)
C(13)	28(2)	60(3)	40(3)	22(3)	2(2)	-5(2)
C(14)	21(2)	59(3)	31(3)	9(2)	4(2)	-1(2)
C(15)	22(2)	41(2)	23(2)	1(2)	-2(2)	-1(2)
C(17)	19(2)	31(2)	27(2)	-2(2)	4(2)	0(2)
C(18)	20(2)	33(2)	23(2)	-2(2)	4(2)	1(2)
C(19)	31(2)	32(2)	23(2)	10(2)	8(2)	4(2)

C(20)	34(3)	36(3)	38(3)	2(2)	14(2)	-15(2)
C(21)	32(2)	28(2)	48(3)	-15(2)	8(2)	-17(2)
C(22)	29(2)	34(2)	20(2)	-3(2)	-3(2)	-10(2)
C(23)	15(2)	42(3)	26(2)	10(2)	-1(2)	2(2)
C(24)	23(2)	37(2)	33(2)	5(2)	3(2)	7(2)
C(25)	20(2)	36(2)	33(3)	0(2)	4(2)	-1(2)
F(1)	43(2)	44(2)	100(3)	-25(2)	3(2)	-9(1)
F(2)	45(2)	73(2)	37(2)	8(2)	8(1)	0(2)
F(3)	29(1)	51(2)	59(2)	8(2)	-5(1)	-2(1)
F(4)	55(2)	40(1)	44(2)	10(1)	6(1)	2(2)
B(1)	29(2)	26(2)	39(3)	3(2)	-1(3)	-8(2)

Table S8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for k08228(CCDC 730 876).

	x	y	z	U(eq)
H(2A)	1291	6439	5035	32
H(2B)	2416	6476	5057	32
H(3A)	1769	7945	4791	43
H(3B)	2389	8029	5359	43
H(4A)	995	8870	5518	46
H(4B)	360	7999	5321	46
H(5A)	416	8062	6335	39
H(5B)	1546	8002	6316	39
H(6A)	390	6589	5819	31
H(7A)	19	6586	6774	35
H(8A)	-9	5148	6266	35
H(8B)	244	4965	6926	35
H(9A)	1338	4171	6314	29
H(10A)	2332	5030	5706	30
H(10B)	1247	5134	5534	30
H(11A)	2760	4717	6741	29

H(12A)	1164	4336	7450	41
H(12B)	1915	3593	7218	41
H(13A)	2193	3926	8205	51
H(13B)	3092	4217	7830	51
H(14A)	2684	5432	8469	44
H(14B)	1657	5492	8185	44
H(15A)	2642	6651	7793	34
H(15B)	3391	5876	7608	34
H(17A)	1460	7111	7187	31
H(17B)	1026	6219	7501	31
H(18A)	3640(30)	5850(30)	5362(14)	31
H(19A)	3620(30)	7400(30)	5466(17)	34
H(20A)	4840	8261	5769	43
H(20B)	5420	7313	5855	43
H(21A)	5399	7799	6757	43
H(21B)	4420	8341	6683	43
H(22A)	4120(30)	7090(30)	7241(6)	33
H(23A)	4250(30)	5580(20)	7014(15)	33
H(24A)	5489	5098	6515	37
H(24B)	5699	6154	6325	37
H(25A)	5290	5517	5478	36
H(25B)	4538	4823	5761	36

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[1] Molecular pictures made using ChemCraft: Grigoriy A. Zhurko., Chemcraft 1.6. http://www.chemcraftprog.com/index.html.

[2] a) M. Suenaga, *J. Comput. Chem. Jpn.*, **2005**, 4, 25. b) M. Suenaga, *J. Comput. Chem. Jpn.*, **2008**, 7,33.

[3] Graphics made, using Molekel: *Molekel 5.3.0.6,* Swiss National Supercomputing Centre, Manno, Switzerland. **2009**.