SUPPLAMENTAL INFORMATION

Ligand K-edge XAS, DFT, and TDDFT Analysis of Pincer Linker Variations in Rh(I) PNP Complexes: Reactivity Insights from Electronic Structure

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Complete reference 20: Gaussian 09, Revision B.01, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li,X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J.A., Jr.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N.J.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, Ö.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J. Gaussian, Inc., Wallingford CT, 2009.

Figure S1. Complete curve fit model of the P K-edge XAS spectrum of Rh(^{tBu}PONOP)Cl (**1**).

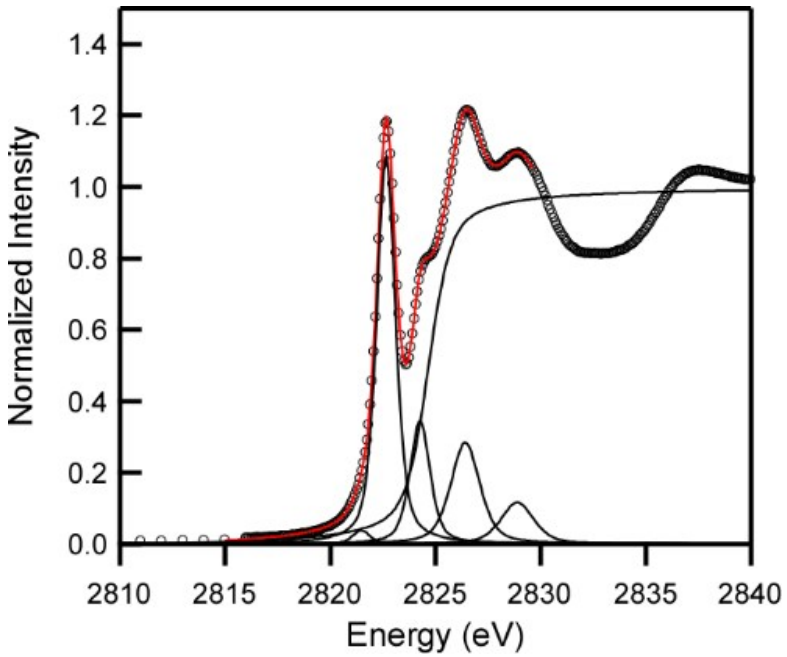

Figure S2. Complete curve fit model of the P K-edge XAS spectrum of Rh(^{tBu}PNP)Cl (**2**).

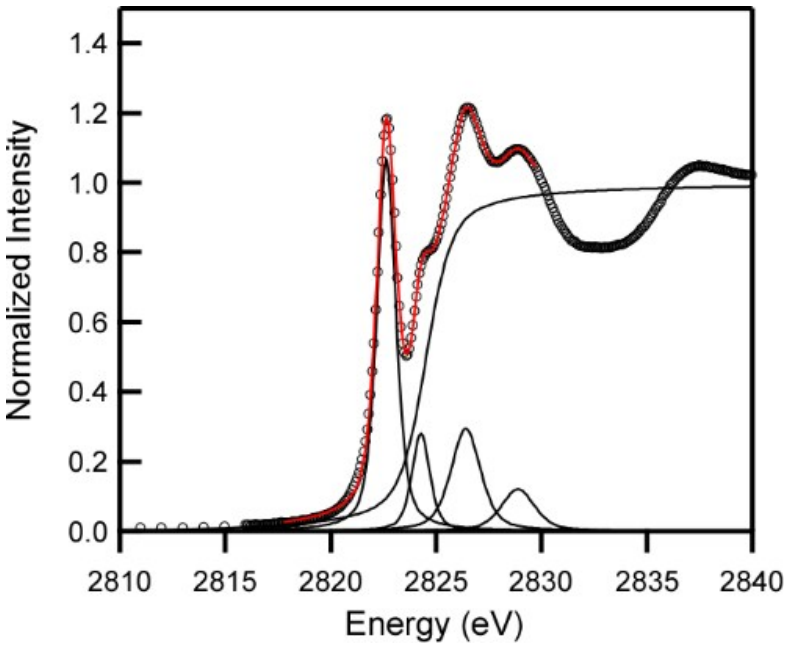

Figure S3. Complete curve fit model of the Cl K-edge XAS spectrum of Rh(^{tBu}PONOP)Cl (**1**).

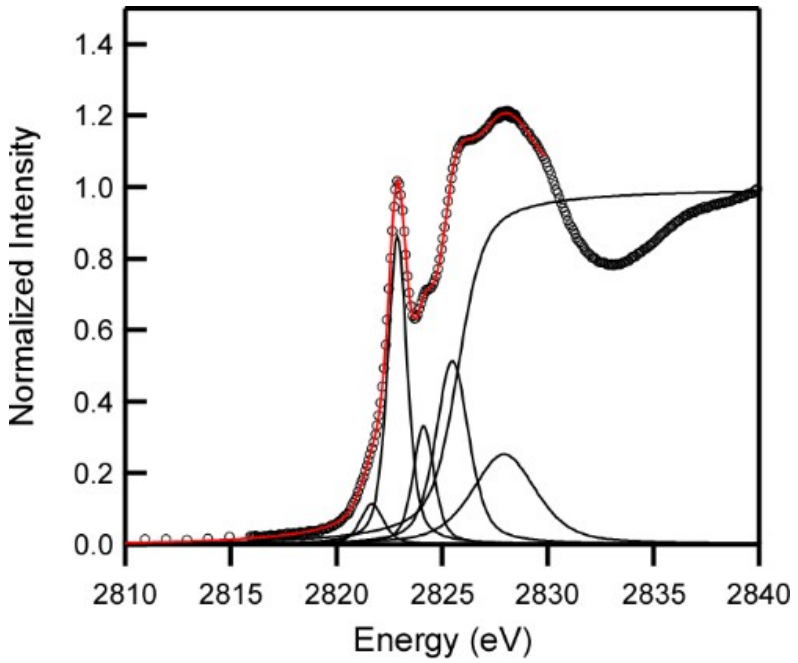

Figure S4. Complete curve fit model of the Cl K-edge XAS spectrum of Rh(^{tBu}PNP)Cl (**2**).

Table S1. Crystallographic data for Rh(^{tBu}PONOP)Cl (**1**).

	1
formula	$C_{21}H_{39}ClNO_2P_2Rh$
FW (g mol^{-1})	537.83
crystal system	triclinic
space group	P-1
a (Å)	8.3122(8)
b (Å)	12.1619(12)
c (Å)	13.3122(13)
α (deg)	100.073(5)
β (deg)	96.132(5)
γ (deg)	104.518(5)
volume (Å^3)	1266.6(2)
Z	2
ρ_{calc} (g cm^{-3})	1.41
μ (mm^{-1})	0.922
F(000)	560
θ range (deg)	1.57/28.07
R(int)	0.0253
data/restraints/parameters	6137/0/266
GOF	1.24
R_1 [$I > 2\sigma(I)$][a]	0.0289
wR_2 (all data)[b]	0.0907
Ext. Coeff	0.0168(10)
Largest Peak and Hole (e·Å^{-3})	0.744/-0.720
Temp (K)	190(1)

[a] $R_1 = \sum |F_o| - |F_c| \, | \, / \, | \sum |F_o|$ for reflections with $F_o^2 > 2\,\sigma(F_o^2)$.

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 \, / \, \sum (F_o^2)^2]^{1/2}$ for all reflections.

Table S2. Calculated (DFT) MO compositions for **1**, **2**, and **2′**.

Compound and Symmetry	MO # and Type	Energy (Hartree)	MO Compositions (%)								
			Rh			P			Cl		
			s	p	d	s	p	d	s	p	d
2′, C_{2v}	136 ($4b_2$)	0.07147	0	0.004	0.015	0.028	0.393	0.044	0	0.003	0
(gas phase)	135 ($5a_1$)	0.07072	0.113	0.329	0.008	-0.008	0.134	0.016	-0.027	-0.001	0
	134 ($4a_1$)	0.0583	0.131	0.021	0.003	-0.044	0.271	0.022	-0.002	-0.002	0
	133 ($4b_1$)	0.04878	0	0.617	0.001	0	0.128	0.02	0	-0.002	0
	132 ($3b_2$)	0.04159	0	0.933	0	-0.054	0.016	0.002	0	-0.003	0
	131 ($3a_1$)	0.03636	0.04	0.65	0.01	-0.006	0.078	0.016	-0.011	0	0
	130 ($3b_1$)	0.0285	0	0.514	0.002	0	0.234	0.032	0	0.009	0.001
	129 ($2a_1$)	0.00742	-0.014	0.02	0.445	0.062	0.186	0.02	-0.006	0.1	0.002
	128 ($2a_2$)	-0.02728	0	0	0.006	0	0.006	0	0	0	0
LUMO	127 ($2b_1$)	-0.04124	0	0.011	0.07	0	0.01	0	0	0.007	0
HOMO	126 ($1a_1$)	-0.15441	0.105	0.001	0.796	0.013	0.036	0.002	0	0.011	0
	125 ($1b_1$)	-0.16069	0	0.006	0.721	0	0.004	0.002	0	0.152	0.001
	124 ($2b_2$)	-0.18027	0	0.002	0.413	0.016	0.082	0.006	0	0.403	0.001
	123 ($1a_2$)	-0.18925	0	0	0.871	0	0.012	0.022	0	0	0
	122 ($1b_2$)	-0.2304	0	0.048	0.303	0.05	0.35	0.008	0	0.025	0
	3 (P 1s)	-77.07272	0	0	0	1	0	0	0	0	0
	2 (P 1s)	-77.07272	0	0	0	1	0	0	0	0	0
	1 (Cl 1s)	-101.4173	0	0	0	0	0	0	1	0	0

Compound and Symmetry	MO # and Type	Energy (Hartree)	MO Compositions (%)								
			Rh			P			Cl		
			s	p	d	s	p	d	s	p	d
2, C_2	136 (8b)	0.07546	0	0.012	0.016	0.018	0.444	0.048	0	0.003	0
(gas phase)	135 (7a)	0.07128	0.113	0.393	0.009	-0.006	0.128	0.016	-0.035	-0.001	0
	134 (6a)	0.05986	0.136	-0.002	0.005	-0.046	0.306	0.026	-0.003	-0.001	0
	133 (7b)	0.05046	0	0.691	0	-0.014	0.118	0.016	0	-0.004	0
	132 (6b)	0.04207	0	0.762	-0.002	-0.034	0.12	0.018	0	-0.001	0
	131 (5a)	0.03766	0.067	0.606	0.023	-0.014	0.06	0.012	-0.009	0.005	0
	130 (5b)	0.02416	0	0.687	0.001	-0.004	0.154	0.02	0	0.007	0
	129 (4a)	0.00784	-0.011	0.042	0.425	0.062	0.192	0.022	-0.01	0.096	0.002
	128 (3a)	-0.02503	-0.001	0.001	0.005	0.002	0.012	0	0	0	0
LUMO	127 (4b)	-0.04431	0	0.015	0.077	0	0.012	0.002	0	0.007	0
HOMO	126 (2a)	-0.1559	0.117	0.001	0.792	0.01	0.034	0.002	0	0.011	0
	125 (3b)	-0.16129	0	0.007	0.709	0	0.004	0.002	0	0.161	0.001
	124 (2b)	-0.18004	0	0.002	0.401	0.02	0.088	0.006	0	0.406	0.001
	123 (1a)	-0.1902	0	0	0.873	0	0.012	0.022	0	0	0

	122 (1b)	-0.23165	0	0.047	0.275	0.05	0.364	0.008	0	0.022	0
	3 (P 1s)	-77.07295	0	0	0	1	0	0	0	0	0
	2 (P 1s)	-77.07295	0	0	0	1	0	0	0	0	0
	1 (Cl 1s)	-101.4155	0	0	0	0	0	0	1	0	0

Compound and Symmetry	**MO # and Type**	**Energy (Hartree)**	**MO Compositions (%)**								
			Rh			**P**			**Cl**		
			s	**p**	**d**	**s**	**p**	**d**	**s**	**p**	**d**
1, C_{2v}	136 ($5a_1$)	0.06353	0.311	0.122	-0.001	-0.056	0.062	0.006	-0.033	0.002	0
(gas phase)	135 ($4b_1$)	0.05351	0.001	0.709	0.001	0	0.158	0.024	-0.002	-0.002	0
	134 ($4a_1$)	0.05142	0.057	0.75	0.002	-0.022	0.09	0.008	-0.012	-0.007	0
	133 ($3b_2$)	0.04977	0	0.978	0	-0.064	-0.032	0	0	-0.006	0
	132 ($2b_2$)	0.03234	0	0.018	0.049	-0.004	0.656	0.042	0	0.003	0
	131 ($3b_1$)	0.02362	0.001	0.54	0.032	0.008	0.182	0.026	0	0.013	0.001
	130 ($3a_1$)	0.02152	0.003	0.129	0.182	0.032	0.378	0.028	0.002	0.029	0.002
	129 ($3a_2$)	-0.00607	0	0	0.001	0	0	0.002	0	0	0
	128 ($2a_1$)	-0.01081	-0.01	0.067	0.263	0.038	0.358	0.034	-0.009	0.081	0.001
LUMO	127 ($2b_1$)	-0.03962	0	0.021	0.058	0	0.026	0.004	0	0.007	0
HOMO	126 ($1a_1$)	-0.16898	0.103	0.001	0.791	0.014	0.036	0.002	0	0.015	0
	125 ($1b_1$)	-0.17324	0.001	0.006	0.687	0	0.006	0.002	0	0.187	0.001
	124 ($1b_2$)	-0.19035	0	0.001	0.332	0.024	0.116	0.008	0	0.443	0
	123 ($2a_2$)	-0.20755	0	0	0.852	0	0.012	0.024	0	0.007	0
	122 ($1a_2$)	-0.23667	0	0	0.016	0	0.006	0.004	0	0.001	0
	3 (P 1s)	-77.11857	0	0	0	1	0	0	0	0	0
	2 (P 1s)	-77.11857	0	0	0	1	0	0	0	0	0
	1 (Cl 1s)	-101.4241	0	0	0	0	0	0	1	0	0

Table S3. Calculated (DFT) atomic coordinates and Mulliken charges for **1**, **2**, and **2′**.

Compound 1		Coordinates (Å)			Mulliken Charges
Atom #	**Atom**	**x**	**y**	**z**	
1	Rh	0.000012	-0.463524	-0.017844	-0.383317
2	C	1.165623	2.279322	-0.046465	0.523928
3	C	-1.165637	2.279314	-0.046542	0.523928
4	C	1.207055	3.672367	-0.065201	-0.153273
5	C	-1.207083	3.672358	-0.065279	-0.153272
6	C	-0.000017	4.367012	-0.074379	-0.075427
7	H	2.167742	4.171193	-0.072878	0.122624
8	H	-2.167775	4.171173	-0.073014	0.122625
9	H	-0.00002	5.452311	-0.089244	0.123357
10	N	-0.000006	1.580879	-0.034799	-0.576482
11	P	-2.260196	-0.141025	0.001842	0.849217
12	P	2.26019	-0.141018	0.001865	0.84923
13	C	-3.279212	-0.504254	-1.560186	-0.140638
14	C	-3.214264	-0.445305	1.617711	-0.138273
15	C	3.279086	-0.504116	-1.560288	-0.140635
16	C	3.21436	-0.445423	1.617667	-0.138276
17	C	2.335285	-0.167378	-2.737739	-0.331893
18	H	2.845371	-0.403771	-3.679522	0.102583
19	H	1.409318	-0.745752	-2.686884	0.164336
20	H	2.074677	0.89568	-2.757299	0.119347

21	C	4.560914	0.336693	-1.703665	-0.306516
22	H	5.330083	0.059592	-0.981427	0.106664
23	H	4.979596	0.174772	-2.704586	0.102968
24	H	4.355656	1.405224	-1.596579	0.118511
25	C	3.59815	-2.012865	-1.59562	-0.340416
26	H	2.706253	-2.621786	-1.413844	0.16215
27	H	3.987973	-2.27128	-2.587606	0.107531
28	H	4.364007	-2.287892	-0.864785	0.108156
29	C	-2.335423	-0.167889	-2.737759	-0.331889
30	H	-2.074517	0.895095	-2.757421	0.119352
31	H	-1.409611	-0.746515	-2.686945	0.164331
32	H	-2.845661	-0.404204	-3.679479	0.10258
33	C	-4.560904	0.336739	-1.703654	-0.306518
34	H	-4.979682	0.174668	-2.704511	0.102968
35	H	-5.330075	0.059945	-0.981299	0.106665
36	H	-4.355439	1.405251	-1.596808	0.118514
37	C	-3.598532	-2.012947	-1.595246	-0.340416
38	H	-3.9883	-2.271492	-2.58722	0.107535
39	H	-2.706751	-2.621989	-1.413288	0.162141
40	H	-4.364498	-2.287705	-0.864428	0.108158
41	C	-4.657881	0.084997	1.636976	-0.30643
42	H	-5.324017	-0.510589	1.008043	0.110836
43	H	-5.045446	0.02715	2.661656	0.103262

44	H	-4.716354	1.129668	1.317952	0.116481
45	C	-3.188414	-1.96094	1.911023	-0.338368
46	H	-3.577331	-2.130794	2.922517	0.10454
47	H	-3.817342	-2.527458	1.219798	0.111611
48	H	-2.175368	-2.369643	1.856327	0.166423
49	C	-2.397008	0.280569	2.710629	-0.337641
50	H	-1.353195	-0.047099	2.708608	0.158858
51	H	-2.420449	1.366799	2.583323	0.117869
52	H	-2.83066	0.047227	3.690254	0.105499
53	C	3.188615	-1.961085	1.910776	-0.338368
54	H	3.817447	-2.527494	1.219366	0.111611
55	H	3.577698	-2.131078	2.922182	0.104539
56	H	2.175583	-2.369832	1.85615	0.166421
57	C	4.657948	0.084968	1.636902	-0.306427
58	H	5.045576	0.027006	2.661553	0.103261
59	H	5.324076	-0.510495	1.00785	0.110835
60	H	4.716334	1.129685	1.318024	0.116481
61	C	2.397136	0.280299	2.710705	-0.337635
62	H	2.420523	1.366537	2.583491	0.117872
63	H	1.35334	-0.047429	2.708731	0.158854
64	H	2.830862	0.046872	3.690277	0.105499
65	Cl	0.000073	-2.857131	-0.06265	-0.454316
66	O	-2.324017	1.591748	-0.041538	-0.606859

67	O	2.324011	1.591767	-0.041364	-0.606864

Compound 2		Coordinates (Å)			Mulliken Charges
Atom #	Atom	x	y	z	
1	Rh	-0.000003	-0.339977	0.000047	-0.301141
2	Cl	0.000003	-2.740198	0.000027	-0.460439
3	P	-2.282024	-0.11348	-0.086907	0.605898
4	N	0.000003	1.721168	0.000041	-0.544169
5	C	-2.359916	1.646926	-0.710376	-0.448296
6	H	-2.359399	1.561801	-1.80312	0.167842
7	H	-3.273738	2.181816	-0.432229	0.134927
8	C	-1.133241	2.425765	-0.30747	0.289091
9	C	-1.155604	3.818927	-0.300286	-0.135181
10	H	-2.079954	4.330849	-0.546987	0.110149
11	C	0.000017	4.534207	0.000038	-0.064889
12	H	0.000022	5.619573	0.000035	0.11605
13	C	-3.148837	-0.066346	1.609284	-0.116144
14	C	-4.6647	0.180327	1.55472	-0.305485
15	H	-5.053955	0.285352	2.575287	0.099461
16	H	-5.198332	-0.650066	1.086845	0.113693
17	H	-4.916305	1.099237	1.013863	0.099826
18	C	-2.481075	1.077247	2.405995	-0.336685
19	H	-2.701757	2.064895	1.988321	0.100407

20	H	-1.394598	0.952665	2.44044	0.158417
21	H	-2.861734	1.064637	3.434416	0.102723
22	C	-2.845973	-1.39266	2.338869	-0.32845
23	H	-1.771746	-1.595893	2.354514	0.166486
24	H	-3.335478	-2.248152	1.870287	0.112973
25	H	-3.209101	-1.326275	3.372308	0.093654
26	C	-3.302257	-1.068703	-1.380614	-0.130193
27	C	-2.364016	-1.254226	-2.595402	-0.324004
28	H	-2.909034	-1.78094	-3.389069	0.094468
29	H	-1.482272	-1.838991	-2.323572	0.170152
30	H	-2.023663	-0.298593	-3.00959	0.105084
31	C	-3.655641	-2.464603	-0.830511	-0.332033
32	H	-4.406877	-2.416154	-0.037211	0.101252
33	H	-2.766449	-2.976612	-0.45192	0.161735
34	H	-4.078892	-3.070292	-1.641425	0.097273
35	C	-4.581379	-0.340898	-1.839352	-0.310221
36	H	-4.36589	0.628991	-2.298856	0.10014
37	H	-5.293939	-0.180675	-1.028436	0.104978
38	H	-5.083204	-0.951359	-2.600408	0.103357
39	P	2.282021	-0.113483	0.086906	0.6059
40	C	2.359928	1.646902	0.71043	-0.448295
41	H	2.359416	1.561745	1.803172	0.167843
42	H	3.273751	2.181796	0.432292	0.134925

43	C	1.133256	2.425755	0.307548	0.28909
44	C	1.155633	3.818917	0.300361	-0.135181
45	H	2.079989	4.330831	0.547054	0.110149
46	C	3.14877	-0.066285	-1.609314	-0.116142
47	C	4.66464	0.180353	-1.554789	-0.305486
48	H	5.053863	0.285422	-2.575365	0.099461
49	H	5.198271	-0.650075	-1.086975	0.113694
50	H	4.916284	1.099229	-1.013894	0.099827
51	C	2.481001	1.077366	-2.405936	-0.336685
52	H	2.701709	2.064985	-1.988207	0.100407
53	H	1.394521	0.952803	-2.440357	0.158415
54	H	2.861629	1.064814	-3.434369	0.102722
55	C	2.845852	-1.392558	-2.33895	-0.32845
56	H	1.771619	-1.595764	-2.354574	0.166485
57	H	3.335349	-2.248082	-1.87042	0.112974
58	H	3.208952	-1.326135	-3.372396	0.093653
59	C	3.302312	-1.068753	1.38053	-0.130192
60	C	2.364129	-1.254322	2.595357	-0.324004
61	H	2.909182	-1.781071	3.388975	0.094468
62	H	1.482369	-1.839072	2.323545	0.170152
63	H	2.023799	-0.298705	3.009601	0.105084
64	C	3.655666	-2.464631	0.830354	-0.332033
65	H	4.40686	-2.416151	0.037015	0.101252

66	H	2.766453	-2.976623	0.451789	0.161736
67	H	4.078959	-3.070353	1.641222	0.097273
68	C	4.581459	-0.340967	1.839227	-0.310221
69	H	4.365995	0.628902	2.298785	0.10014
70	H	5.293973	-0.180707	1.028278	0.104977
71	H	5.083328	-0.95146	2.600228	0.103356

Compound 2′		**Coordinates (Å)**			**Mulliken Charges**
Atom #	**Atom**	**x**	**y**	**z**	
1	Rh	-0.000004	-0.287181	0.000003	-0.302739
2	C	1.170864	2.49721	0.003939	0.281178
3	C	-1.170916	2.497188	-0.0027	0.281174
4	C	1.189249	3.891121	0.005136	-0.129317
5	C	-1.189333	3.891099	-0.002795	-0.129316
6	C	-0.00005	4.610511	0.001186	-0.064611
7	H	2.148344	4.399273	0.008553	0.109235
8	H	-2.148441	4.399228	-0.005841	0.109235
9	H	-0.000059	5.695856	0.00151	0.116134
10	N	-0.000024	1.78473	0.000544	-0.524221
11	P	-2.292456	-0.094911	-0.006651	0.630665
12	P	2.292364	-0.094809	0.006758	0.630639
13	C	-2.492225	1.764737	-0.006863	-0.462848
14	H	-3.089797	2.089552	0.849733	0.149577

15	H	-3.054598	2.074461	-0.893197	0.149665
16	C	2.492188	1.764784	0.008889	-0.46282
17	H	3.053257	2.073548	0.896396	0.149713
18	H	3.091049	2.090416	-0.846494	0.149532
19	C	-3.221467	-0.634189	-1.582397	-0.128837
20	C	-3.193749	-0.60642	1.598926	-0.129477
21	C	3.193547	-0.604704	-1.599351	-0.12945
22	C	3.221637	-0.635774	1.581804	-0.128841
23	C	2.422737	0.100421	-2.740883	-0.33354
24	H	2.827488	-0.235063	-3.703333	0.101622
25	H	1.357066	-0.146074	-2.706881	0.163344
26	H	2.519523	1.190831	-2.711735	0.101611
27	C	4.678619	-0.205075	-1.660019	-0.305834
28	H	5.288002	-0.812995	-0.987007	0.111454
29	H	5.056737	-0.371206	-2.676395	0.100809
30	H	4.849971	0.848973	-1.416516	0.097814
31	C	3.059921	-2.125698	-1.816198	-0.322034
32	H	2.020908	-2.454403	-1.745901	0.16443
33	H	3.443815	-2.375629	-2.813474	0.090904
34	H	3.640785	-2.698945	-1.09095	0.10255
35	C	-2.316285	-0.173861	-2.748618	-0.328564
36	H	-2.17477	0.912798	-2.763142	0.10622
37	H	-1.328791	-0.639036	-2.68587	0.166141

38	H	-2.782003	-0.459525	-3.700128	0.097837
39	C	-4.624186	-0.026134	-1.768481	-0.307551
40	H	-5.0297	-0.358018	-2.732291	0.103299
41	H	-5.32363	-0.344075	-0.993868	0.106857
42	H	-4.614197	1.068477	-1.787157	0.097889
43	C	-3.317574	-2.172538	-1.617658	-0.328631
44	H	-3.6125	-2.489502	-2.625777	0.095437
45	H	-2.362043	-2.644219	-1.371355	0.164886
46	H	-4.079048	-2.544626	-0.926689	0.100486
47	C	-4.67852	-0.205692	1.660483	-0.305834
48	H	-5.288547	-0.812044	0.986661	0.111425
49	H	-5.056545	-0.373098	2.676688	0.100815
50	H	-4.849091	0.848871	1.418689	0.097813
51	C	-3.061313	-2.127805	1.813543	-0.32205
52	H	-3.444758	-2.378828	2.810713	0.090923
53	H	-3.643223	-2.699466	1.087876	0.102506
54	H	-2.022629	-2.457324	1.742094	0.164435
55	C	-2.42218	0.09655	2.741249	-0.333509
56	H	-1.356768	-0.151016	2.70697	0.163373
57	H	-2.517768	1.187101	2.71332	0.101623
58	H	-2.8273	-0.23957	3.703321	0.101605
59	C	3.31903	-2.174084	1.614589	-0.32865
60	H	4.08083	-2.544382	0.923003	0.100493

61	H	3.614237	-2.492435	2.622183	0.095442
62	H	2.36387	-2.646186	1.367587	0.164867
63	C	4.623826	-0.026791	1.769029	-0.307579
64	H	5.02972	-0.360331	2.73211	0.103306
65	H	5.323537	-0.342336	0.99369	0.106853
66	H	4.612748	1.067764	1.790102	0.097888
67	C	2.315952	-0.178014	2.748596	-0.328525
68	H	2.173657	0.908522	2.764755	0.106232
69	H	1.328813	-0.643804	2.684891	0.166153
70	H	2.7817	-0.464833	3.699749	0.09782
71	Cl	0.00019	-2.688348	-0.000621	-0.459131