Synthesis and Characterization of Rhodium complexes with Phosphine-stabilized Germylenes

Supporting Information

Juan Manuel García,[‡] Edgar Ocando-Mavárez,*[‡] Tsuyoshi Kato,[†] David Santiago Coll,[§] Alexander Briceño,[#] Nathalie Saffon-Merceron,[Δ] and Antoine Baceiredo*[†]

Theoretical Calculation Data

All structures were optimized using DMol[3]. This DFT Based program allows us to determine the relative stability of all studied species based on their electronic structure. The calculations were performed using Kohn-Sham Hamiltonian with the Perdew-Wang 1991 gradient correction and the double-zeta plus (DNP) numerical basic set. The utilization of the numerical basics sets combined with DFT allows the program to obtain a high accuracy by keeping a relative low computational cost, compared with ab-initio methods. DMol[3] calculates variational self-consistent solutions to the density functional theory (DFT) equations. The solutions to these equations provide the molecular electron densities, which can be integrated among the atomic volume (defined by the interatomic surfaces and/or the Van der Walls envelope) in order to obtain the Bader charge on each atom of the system.

Cartesian coordinates.

1a

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Cl1	6.0919	19.4372	10.6220
2	Ge2	4.1225	19.6739	11.8179
3	P3	3.8718	17.2036	12.2363
4	C4	2.2572	18.0563	10.2671
5	N5	4.9815	15.9080	12.2740
6	H6	0.5301	18.3445	8.8957
7	H7	1.1488	16.3749	7.5026
8	C8	2.2583	15.3827	9.1385
9	H9	1.7366	14.4812	8.7861
10	H10	3.3357	15.1841	9.1092
11	C11	1.7889	15.7727	10.5690
12	C12	5.9472	15.6594	11.1855
13	H13	5.6004	16.2728	10.3412
14	C14	7.3693	16.1038	11.5385
15	H15	7.3884	17.1640	11.8185
16	H16	8.0296	15.9702	10.6713
17	H17	7.7821	15.5044	12.3632
18	C18	5.9040	14.1869	10.7609
19	H19	6.2555	13.5274	11.5672
20	H20	6.5566	14.0205	9.8935
21	H21	4.8826	13.8873	10.4939
22	C22	2.1501	20.3972	9.6414
23	C23	2.6416	20.8735	8.4024
24	C24	2.0112	21.9777	7.8142
25	H25	2.3765	22.3508	6.8567
26	H26	0.4628	23.4738	7.9557
27	C27	0.5286	20.5925	11.6380
28	H28	1.0985	19.7047	11.9416
29	C29	0.7467	21.6684	12.7152
30	H30	0.4091	21.3032	13.6963
31	H31	0.1808	22.5824	12.4848
32	C32	2.6430	16.9469	11.0385
33	N33	2.7971	19.2879	10.2857

34	N34	3.4957	16.9745	13.8955
35	C35	1.1531	17.5630	9.3414
36	C36	1.8590	16.6320	8.3002
37	H37	2.7206	17.1230	7.8341
38	H38	1.7243	14.9324	11.2697
39	C39	0.4698	16.5126	10.2444
40	H40	-0.0020	16.9527	11.1325
41	H41	-0.2612	15.8957	9.7007
42	C42	2.6746	18.1579	15.9058
43	H43	2.8637	17.3307	16.6044
44	H44	1.8372	18.7432	16.3092
45	H45	3.5654	18.7975	15.8741
46	C46	1.0723	16.7692	14.5085
47	H47	0.8316	16.4263	13.4945
48	H48	0.2148	17.3377	14.8937
49	H49	1.2009	15.8878	15.1530
50	C50	2.3350	17.6406	14.5055
51	H51	2.1386	18.5189	13.8699
52	C52	3.9708	15.6861	14.3987
53	H53	3.2598	14.8627	14.1999
54	H54	4.1506	15.7365	15.4811
55	C55	5.2705	15.4535	13.6348
56	H56	6.0930	16.0231	14.1017
57	H57	5.5430	14.3886	13.6288
58	C58	0.9356	22.6121	8.4284
59	C59	0.4716	22.1456	9.6559
60	H60	-0.3647	22.6517	10.1399
61	C61	1.0633	21.0437	10.2845
62	C62	-0.9512	20.1800	11.5655
63	H63	-1.5902	21.0317	11.2921
64	H64	-1.2937	19.8051	12.5409
65	H65	-1.1113	19.3905	10.8194
66	C66	3.8290	20.2336	7.6995
67	H67	4.1660	19.3960	8.3240
68	C68	5.0033	21.2187	7.5819
69	H69	4.7390	22.0795	6.9499
70	H70	5.8731	20.7213	7.1301
71	H71	5.3071	21.5926	8.5670
72	C72	3.4430	19.6855	6.3159
73	H73	2.6125	18.9696	6.3792
74	H74	4.3017	19.1774	5.8538
75	H75	3.1317	20.4936	5.6382
76	H76	1.8083	21.9374	12.7940

1b

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Ge1	3.9696	9.6705	0.9071
2	P2	4.3605	9.1605	3.2810
3	N3	4.1154	7.6415	0.6616
4	N4	3.2851	9.9863	4.3381
5	N5	5.6912	9.5232	4.3143
6	C6	3.9095	7.4947	3.0905
7	C7	3.9133	6.9546	1.7918
8	C8	3.5108	5.4935	1.9350
9	H9	3.7461	4.8558	1.0771
10	C10	1.9974	5.5061	2.3325
11	H11	1.4034	6.1205	1.6461
12	H12	1.5978	4.4834	2.2928
13	C13	2.0073	6.0611	3.7868
14	H14	1.3986	6.9659	3.8997
15	H15	1.6371	5.3112	4.5013
16	C16	3.5170	6.3565	4.0269

17	H17	3.7846	6.4979	5.0801
18	C18	4.1601	5.1548	3.2949
19	H19	5.2559	5.2035	3.2713
20	H20	3.8374	4.1786	3.6862
21	C21	1.8108	11.7600	3.3379
22	H22	2.0235	12.5187	4.1041
23	H23	0.7933	11.9407	2.9658
24	H24	2.5044	11.9016	2.4982
25	C25	0.9201	10.1000	5.0396
26	H26	1.0007	9.0718	5.4140
27	H27	-0.1059	10.2663	4.6847
28	H28	1.0912	10.7871	5.8804
29	C29	1.9218	10.3407	3.9051
30	H30	1.6867	9.6359	3.0922
31	C31	3.9961	10.8495	5.2776
32	H32	3.3932	11.0088	6.1828
33	H33	4.2427	11.8373	4.8460
34	C34	5.2790	10.0892	5.5987
35	H35	6.0487	10.7676	5.9920
36	H36	5.0795	9.3093	6.3559
37	C37	6.9686	8.8012	4.1885
38	H38	7.0049	8.4630	3.1413
39	C39	7.0523	7.5648	5.0943
40	H40	7.0368	7.8499	6.1561
41	H41	7.9910	7.0226	4.9144
42	H42	6.2165	6.8811	4.9056
43	C43	8.1589	9.7357	4.4246
44	H44	8.1155	10.6092	3.7629
45	H45	9.1009	9.2046	4.2334
46	H46	8.1893	10.0878	5.4654
47	C47	4.3083	7.0190	-0.6100
48	C48	3.2513	6.9969	-1.5523
49	C49	3.4915	6.4378	-2.8141
50	H50	2.6858	6.4164	-3.5487
51	C51	4.7343	5.9048	-3.1443
52	H52	4.9000	5.4693	-4.1303
53	C53	5.7645	5.9286	-2.2076
54	H54	6.7363	5.5104	-2.4719
55	C55	5.5824	6.4882	-0.9369
56	C56	1.8653	7.5388	-1.2322
57	H57	1.8738	7.8563	-0.1805
58	C58	1.5265	8.7778	-2.0772
59	H59	2.2475	9.5868	-1.8989
60	H60	0.5266	9.1545	-1.8191
61	H61	1.5327	8.5428	-3.1515
62	C62	0.7815	6.4583	-1.3894
63	H63	0.6785	6.1390	-2.4363
64	H64	-0.1935	6.8488	-1.0645
65	H65	1.0139	5.5676	-0.7904
66	C66	6.7414	6.4922	0.0517
67	H67	6.4258	7.0867	0.9190
68	C68	8.0021	7.1551	-0.5254
69	H69	8.4023	6.5863	-1.3770
70	H70	8.7895	7.1966	0.2413
71	H71	7.7959	8.1783	-0.8600
72	C72	7.0609	5.0676	0.5382
73	H73	6.1843	4.5850	0.9887
74	H74	7.8654	5.0875	1.2878
75	H75	7.3977	4.4356	-0.2964
76	C76	5.7578	10.2971	0.1839
77	C77	5.9528	10.2746	-1.2083
78	H78	5.2211	9.7831	-1.8537
79	C79	7.0756	10.8684	-1.7926

80	H80	7.2101	10.8279	-2.8745
81	C81	8.0199	11.5184	-0.9936
82	H82	8.8946	11.9861	-1.4467
83	C83	7.8330	11.5669	0.3899
84	H84	8.5648	12.0748	1.0208
85	C85	6.7118	10.9638	0.9697
86	H86	6.5803	11.0139	2.0518

2a

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Rh1	22.1219	-1.9803	2.7013
2	Ge2	23.8976	-2.4399	4.3634
3	Cl3	23.2917	-3.5037	1.2358
4	P4	24.2669	-4.7310	5.1796
5	N5	25.8741	-2.4064	4.0008
6	N6	24.0752	-5.0400	6.8405
7	N7	23.2458	-6.0135	4.7589
8	C8	20.7485	-1.3301	4.2457
9	H9	21.1555	-1.6316	5.2151
10	C10	21.3264	-0.1851	3.6552
11	H11	22.1510	0.2759	4.2044
12	C12	20.6019	0.7254	2.6720
13	H13	20.9493	1.7576	2.8184
14	H14	19.5274	0.7351	2.9054
15	C15	20.8303	0.3279	1.1982
16	H16	20.0164	0.7248	0.5638
17	H17	21.7535	0.8034	0.8397
18	C18	20.9774	-1.1602	0.9844
19	H19	21.5986	-1.4577	0.1362
20	C20	20.1917	-2.1559	1.5643
21	H21	20.2757	-3.1570	1.1358
22	C22	18.9968	-1.8931	2.4610
23	H23	18.2410	-2.6718	2.2870
24	H24	18.5255	-0.9437	2.1722
25	C25	19.3660	-1.8758	3.9597
26	H26	18.6068	-1.3113	4.5331
27	H27	19.3300	-2.9049	4.3467
28	C28	23.3707	-6.2955	7.1070
29	H29	24.0667	-7.1495	7.1926
30	H30	22.7910	-6.2217	8.0366
31	C31	22.4543	-6.4757	5.9022
32	H32	21.5275	-5.8894	6.0324
33	H33	22.1826	-7.5308	5.7632
34	C34	22.7784	-6.2759	3.3811
35	H35	23.3911	-5.6413	2.7253
36	C36	21.3202	-5.8649	3.1705
37	H37	21.1765	-4.8035	3.4162
38	H38	21.0511	-5.9958	2.1146
39	H39	20.6330	-6.4754	3.7756
40	C40	23.0213	-7.7420	3.0094
41	H41	24.0755	-8.0117	3.1547
42	H42	22.4040	-8.4227	3.6144
43	H43	22.7605	-7.9101	1.9559
44	C44	24.9406	-4.4251	7.8621
45	H45	25.3741	-3.5382	7.3799
46	C46	26.0854	-5.3486	8.2957
47	H47	26.6887	-5.6609	7.4331
48	H48	26.7428	-4.8295	9.0065
49	H49	25.7054	-6.2499	8.7977
50	C50	24.1146	-3.9370	9.0544
51	H51	23.3258	-3.2545	8.7164
52	H52	23.6537	-4.7741	9.5984

53	H53	24.7570	-3.3992	9.7645
54	C54	25.8261	-4.8321	4.4441
55	C55	26.4246	-3.6352	4.0126
56	C56	27.7868	-4.0203	3.4610
57	H57	28.4992	-3.1966	3.3560
58	C58	27.4850	-4.7882	2.1289
59	H59	28.4263	-4.9462	1.5851
60	H60	26.8068	-4.2252	1.4790
61	C61	26.8688	-6.1328	2.6140
62	H62	25.8703	-6.3057	2.1973
63	H63	27.5057	-6.9867	2.3406
64	C64	26.8268	-5.9473	4.1588
65	H65	26.6729	-6.8722	4.7259
66	C66	28.1557	-5.1954	4.3936
67	H67	29.0397	-5.7467	4.0419
68	H68	28.2966	-4.8918	5.4387
69	C69	26.6601	-1.2105	3.8247
70	C70	27.4226	-0.7090	4.9124
71	C71	28.1487	0.4737	4.7297
72	H72	28.7411	0.8645	5.5578
73	C73	28.1267	1.1623	3.5207
74	H74	28.6931	2.0869	3.4041
75	C75	27.3794	0.6573	2.4627
76	H76	27.3724	1.1862	1.5088
77	C77	26.6466	-0.5304	2.5832
78	C78	27.5149	-1.4112	6.2606
79	H79	26.7906	-2.2347	6.2541
80	C80	28.9169	-2.0079	6.4833
81	H81	29.2134	-2.6782	5.6669
82	H82	29.6731	-1.2120	6.5494
83	H83	28.9480	-2.5765	7.4241
84	C84	27.1463	-0.4829	7.4290
85	H85	26.1578	-0.0337	7.2790
86	H86	27.1277	-1.0501	8.3708
87	H87	27.8815	0.3259	7.5470
88	C88	25.9075	-1.0546	1.3650
89	H89	25.4013	-1.9875	1.6400
90	C90	24.8183	-0.0806	0.8934
91	H91	24.2786	-0.5132	0.0404
92	H92	24.0875	0.1028	1.6936
93	H93	25.2437	0.8851	0.5811
94	C94	26.8786	-1.3773	0.2159
95	H95	27.6804	-2.0528	0.5433
96	H96	26.3345	-1.8634	-0.6060
97	H97	27.3508	-0.4669	-0.1821
98	Cl98	23.7984	-1.2859	6.3239

2b

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Rh1	22.2002	-2.1100	2.5683
2	Ge2	23.8967	-2.2745	4.3970
3	Cl3	23.5100	-3.5897	1.1753
4	P4	24.2103	-4.5343	5.2839
5	N5	25.8698	-2.3283	3.9814
6	N6	24.0664	-4.8331	6.9749
7	N7	23.1319	-5.7885	4.9255
8	C8	20.6997	-1.4721	3.9915
9	H9	21.0346	-1.7124	5.0054
10	C10	21.2689	-0.3208	3.4012
11	H11	22.0210	0.2025	3.9963
12	C12	20.5670	0.5291	2.3496
13	H13	20.8642	1.5793	2.4822

14	H14	19.4814	0.5033	2.5236
15	C15	20.8929	0.0970	0.9043
16	H16	20.0945	0.4302	0.2160
17	H17	21.8075	0.6101	0.5780
18	C18	21.1270	-1.3872	0.7536
19	H19	21.8164	-1.6832	-0.0404
20	C20	20.3497	-2.3999	1.3121
21	H21	20.5054	-3.4077	0.9223
22	C22	19.0884	-2.1616	2.1202
23	H23	18.3799	-2.9799	1.9288
24	H24	18.5964	-1.2451	1.7664
25	C25	19.3541	-2.0713	3.6391
26	H26	18.5432	-1.5046	4.1339
27	H27	19.3176	-3.0830	4.0682
28	C28	23.3663	-6.0902	7.2543
29	H29	24.0525	-6.9558	7.2752
30	H30	22.8439	-6.0333	8.2190
31	C31	22.3816	-6.2309	6.0996
32	H32	21.4821	-5.6152	6.2820
33	H33	22.0669	-7.2750	5.9705
34	C34	22.6538	-6.1092	3.5651
35	H35	23.2750	-5.5180	2.8773
36	C36	21.2040	-5.6788	3.3432
37	H37	21.1012	-4.5969	3.5070
38	H38	20.9125	-5.8834	2.3048
39	H39	20.5095	-6.2185	4.0046
40	C40	22.8662	-7.5952	3.2602
41	H41	23.9140	-7.8809	3.4199
42	H42	22.2316	-8.2376	3.8893
43	H43	22.6060	-7.8015	2.2133
44	C44	25.0782	-4.3287	7.9226
45	H45	25.4279	-3.3791	7.4914
46	C46	26.2829	-5.2670	8.0729
47	H47	26.7482	-5.4690	7.1009
48	H48	27.0386	-4.8140	8.7295
49	H49	25.9863	-6.2246	8.5240
50	C50	24.4530	-4.0174	9.2857
51	H51	23.5858	-3.3546	9.1825
52	H52	24.1373	-4.9348	9.8019
53	H53	25.1909	-3.5180	9.9274
54	C54	25.7252	-4.7306	4.4726
55	C55	26.3673	-3.5760	3.9957
56	C56	27.6805	-4.0372	3.3854
57	H57	28.4323	-3.2551	3.2439
58	C58	27.2686	-4.7873	2.0729
59	H59	28.1689	-5.0004	1.4800
60	H60	26.5856	-4.1894	1.4595
61	C61	26.6012	-6.0922	2.5949
62	H62	25.5775	-6.2060	2.2234
63	H63	27.1761	-6.9819	2.2997
64	C64	26.6439	-5.9027	4.1402
65	H65	26.4684	-6.8175	4.7177
66	C66	28.0268	-5.2293	4.3035
67	H67	28.8573	-5.8344	3.9117
68	H68	28.2409	-4.9307	5.3374
69	C69	26.7138	-1.1721	3.8427
70	C70	27.5414	-0.7737	4.9276
71	C71	28.2875	0.4041	4.8002
72	H72	28.9222	0.7226	5.6281
73	C73	28.2337	1.1798	3.6453
74	H74	28.8176	2.0978	3.5724
75	C75	27.4383	0.7657	2.5818
76	H76	27.4130	1.3592	1.6672

77	C77	26.6764	-0.4086	2.6499
78	C78	27.6791	-1.5787	6.2144
79	H79	26.9839	-2.4251	6.1540
80	C80	29.1022	-2.1496	6.3575
81	H81	29.3955	-2.7390	5.4799
82	H82	29.8382	-1.3417	6.4773
83	H83	29.1686	-2.7964	7.2446
84	C84	27.3084	-0.7646	7.4653
85	H85	26.2878	-0.3705	7.3999
86	H86	27.3787	-1.3975	8.3624
87	H87	27.9929	0.0836	7.6089
88	C88	25.8822	-0.8417	1.4293
89	H89	25.3236	-1.7503	1.6839
90	C90	24.8542	0.2147	1.0006
91	H91	24.2751	-0.1597	0.1458
92	H92	24.1475	0.4281	1.8143
93	H93	25.3339	1.1584	0.7004
94	C94	26.8184	-1.1946	0.2602
95	H95	27.5568	-1.9525	0.5545
96	H96	26.2325	-1.5966	-0.5779
97	H97	27.3685	-0.3118	-0.0980
98	C98	23.7649	-0.9925	5.9315
99	C99	24.2091	0.3326	5.7812
100	H100	24.7618	0.6290	4.8883
101	C101	23.9673	1.2877	6.7733
102	H102	24.3325	2.3071	6.6417
103	C103	23.2584	0.9402	7.9262
104	H104	23.0659	1.6862	8.6979
105	C105	22.7941	-0.3679	8.0807
106	H106	22.2344	-0.6464	8.9750
107	C107	23.0420	-1.3229	7.0887
108	H108	22.6775	-2.3428	7.2265

3a

Center Number	Atoms	Coordinates (Angstroms) X	Y	Z
1	Rh1	22.6766	17.9520	4.8627
2	Ge2	21.4099	16.7211	3.1868
3	Cl3	21.4210	14.4558	3.3960
4	Cl4	21.9930	16.9126	1.0242
5	P5	20.8512	17.5619	6.2667
6	N6	20.6578	18.7573	7.5446
7	N7	20.9492	16.3144	7.4683
8	N8	19.4771	17.0783	3.0537
9	C9	24.6154	17.9731	3.6159
10	H10	24.4784	17.1129	2.9567
11	C11	23.8757	19.1085	3.3125
12	H12	23.2480	19.0601	2.4196
13	C13	24.0893	20.4934	3.8715
14	H14	24.8621	21.0208	3.2819
15	H15	23.1596	21.0597	3.7180
16	C16	24.4585	20.5285	5.3700
17	H17	24.2151	21.5244	5.7669
18	H18	25.5433	20.4147	5.4980
19	C19	23.7341	19.4862	6.2016
20	H20	22.9192	19.8635	6.8281
21	C21	24.2283	18.2186	6.4945
22	H22	23.7935	17.7006	7.3517
23	C23	25.5177	17.6172	5.9905
24	H24	26.3612	17.9373	6.6302
25	H25	25.4477	16.5269	6.1136
26	C26	25.8375	17.9350	4.5127
27	H27	26.5297	17.1704	4.1336

28	H28	26.3748	18.8899	4.4391
29	C29	20.8045	18.2022	8.8949
30	H30	21.4400	18.8492	9.5150
31	H31	19.8160	18.1173	9.3767
32	C32	21.4439	16.8252	8.7372
33	H33	21.1355	16.1636	9.5589
34	H34	22.5471	16.9090	8.7771
35	C35	21.2868	14.9338	7.0649
36	H36	20.8065	14.7896	6.0864
37	C37	22.7888	14.6882	6.8840
38	H38	23.2003	15.3850	6.1395
39	H39	23.3350	14.8090	7.8315
40	H40	22.9639	13.6669	6.5203
41	C41	20.6675	13.9265	8.0408
42	H42	19.5981	14.1260	8.1864
43	H43	20.7810	12.9091	7.6442
44	H44	21.1631	13.9500	9.0221
45	C45	20.5433	20.1346	7.3434
46	C46	20.3359	20.6293	5.9536
47	H47	20.5203	21.7120	5.9082
48	H48	21.0105	20.1217	5.2383
49	H49	19.3087	20.4514	5.5817
50	C50	20.0766	20.9961	8.4749
51	H51	20.5443	20.7557	9.4383
52	H52	20.2989	22.0484	8.2534
53	H53	18.9787	20.9289	8.6288
54	C54	19.2521	17.4107	5.5450
55	C55	18.8111	17.2714	4.2249
56	C56	17.2842	17.2167	4.2927
57	H57	16.7775	17.4229	3.3460
58	C58	16.9451	15.8200	4.9138
59	H59	17.4620	15.0078	4.3912
60	H60	15.8651	15.6352	4.8332
61	C61	17.3956	15.9704	6.3928
62	H62	18.1435	15.2267	6.6877
63	H63	16.5430	15.8878	7.0833
64	C64	17.9852	17.4071	6.4146
65	H65	18.1260	17.8271	7.4160
66	C66	17.0014	18.1425	5.4863
67	H67	17.2829	19.1871	5.3015
68	H68	15.9557	18.0919	5.8239
69	C69	18.8183	17.3496	1.7955
70	C70	18.7244	18.6920	1.3514
71	C71	18.0870	18.9517	0.1327
72	H72	18.0065	19.9813	-0.2182
73	C73	17.5658	17.9220	-0.6446
74	H74	17.0795	18.1419	-1.5956
75	C75	17.6823	16.6075	-0.2044
76	H76	17.2836	15.7995	-0.8191
77	C77	18.3041	16.2921	1.0100
78	C78	19.3057	19.8616	2.1342
79	H79	19.7626	19.4590	3.0470
80	C80	20.4157	20.5711	1.3384
81	H81	21.1878	19.8594	1.0197
82	H82	20.0117	21.0539	0.4368
83	H83	20.8868	21.3523	1.9529
84	C84	18.2172	20.8613	2.5591
85	H85	17.4254	20.3705	3.1403
86	H86	18.6513	21.6628	3.1740
87	H87	17.7459	21.3312	1.6834
88	C88	18.3946	14.8327	1.4253
89	H89	18.8762	14.7980	2.4100
90	C90	19.2774	14.0277	0.4567

91	H91	19.3901	12.9959	0.8180
92	H92	18.8289	13.9905	-0.5472
93	H93	20.2770	14.4704	0.3720
94	C94	17.0022	14.1867	1.5484
95	H95	16.3502	14.7518	2.2270
96	H96	16.5002	14.1307	0.5715
97	H97	17.0946	13.1612	1.9334

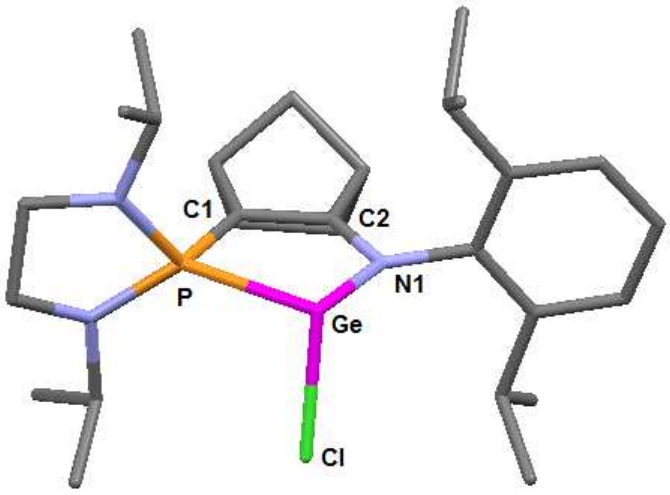


Figure S1. Calculated molecular structure of **1a**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge-Cl 2.316 N1-Ge 2.062, Ge-P 2.518, P-C1 1.735, C1-C2 1.405, C2-N1 1.345, Cl-Ge-P 94.03, Cl-Ge-N1 98.26, N1-Ge-P 82.87, Ge-P-C1 95.79, P1-C1-C2 117.17, C1-C2-N1 127.24, C2-N1-Ge 116.06.

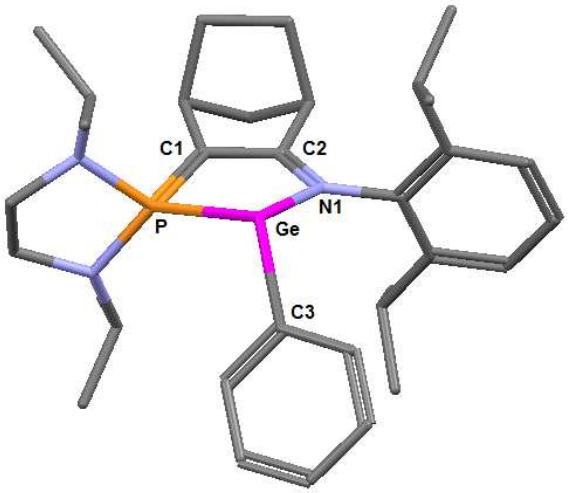


Figure S2. Calculated molecular structure of **1b**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge−P 2.459, Ge−N1 2.049, Ge−C3 2.028, P−C1 1.736; C1−C2 1.407, C2−N1 1.338, N1−Ge−P 84.20, C3−Ge−P 105.55, N1−Ge−C3 101.56, C2−N1−Ge 113.36, N1−C2−C1 125.68, C2−C1−P 117.97, C1−P−Ge 92.97.

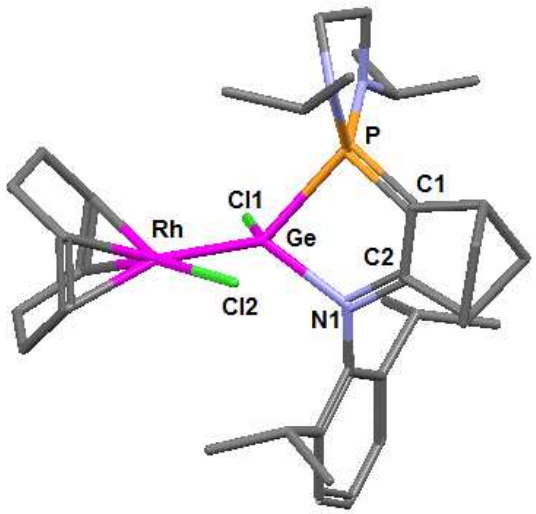


Figure S3. Calculated molecular structure of **2a**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge−Rh 2.475, Ge−P 2.460, Ge−Cl1 2.277, Ge−N1 2.010, N1-C2 1.347, C1−C2 1.406, P−C1 1.727, Rh-Cl2 2.416; Cl2−Rh−Ge 86.73, Cl1−Ge−Rh 116.92, N1−Ge−C3 101.12, C3−Ge−P 100.94, N1-Ge-P 85.86.

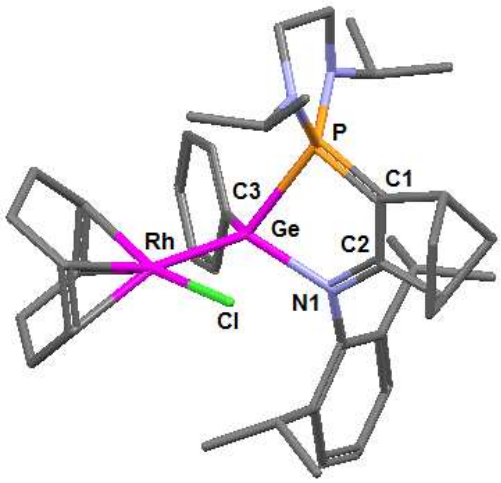


Figure S4. Calculated molecular structure of **2b**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge−Rh 2.500, Ge−P 2.448, Ge−C3 2.004, Ge−N1 2.017, N1-C2 1.343, C1−C2 1.405, P−C1 1.730, Rh-Cl 2.418; Cl−Rh−Ge 90.78, C3−Ge−Rh 108.76, N1−Ge−C3 108.76, C3−Ge−P 103.84, N1-Ge-P 85.68.

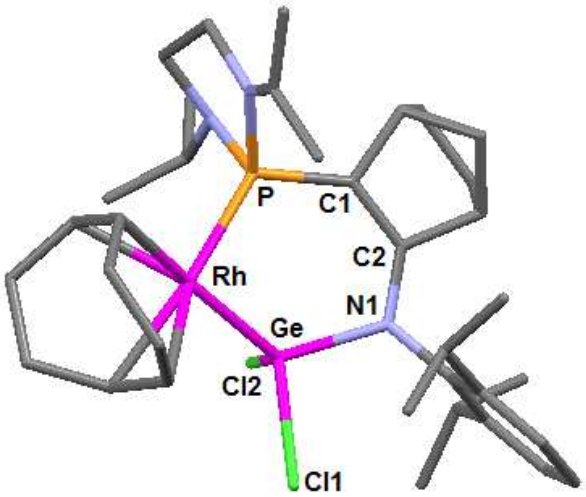


Figure S5. Calculated molecular structure of **3a**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Rh−P 2.336, Rh−Ge 2.435, Ge−Cl1 2.248, Ge−Cl2 2.275, Ge−N1 1.970, N1−C2 1.361, C1−C2 1.399, P−C1 1.761; Cl1−Ge−Cl2 99.91, N1−Ge−Rh 117.73, N1−Ge−Cl2 101.04, N1−Ge−Cl1 100.02, Cl2−Ge−Rh 115.95, Cl1−Ge−Rh 118.96, P−Rh−Ge 85.57.