

## Supporting Information

### Synthesis of a Rhodium(I) Germyl Complex: A Useful Tool for C–H and C–F Bond Activation Reactions

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#### Computational details

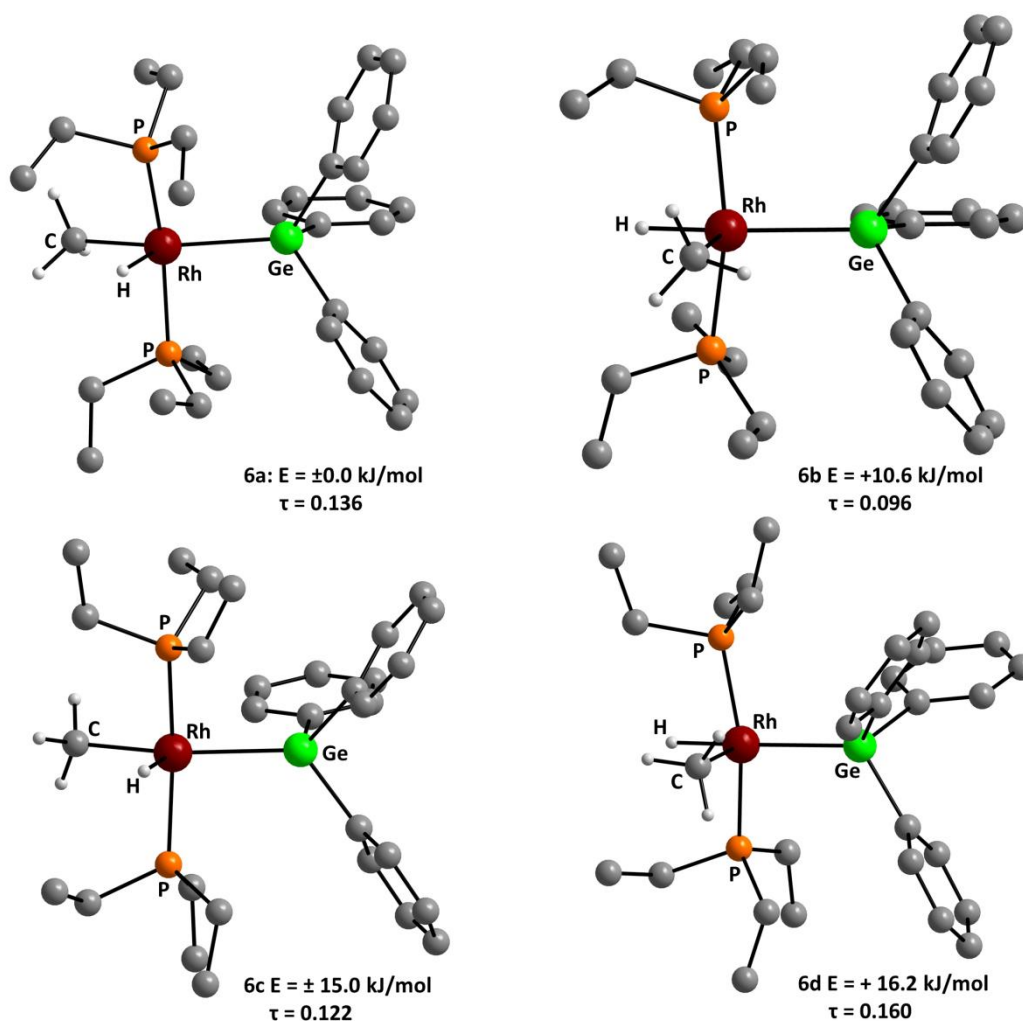
In order to determine the IR absorption bands of complex  $[\text{Rh}(\text{GePh}_3)(\text{H})_2(\text{PEt}_3)_3]$  (**2**) with the help of DFT calculations, the structure of **2** was optimized based on the structure in the solid, which was obtained by a X-ray crystallography analysis. Two absorption bands can be assigned to the metal-bonded hydrido ligands which are in good accordance to the experimental IR-spectrum. For the antisymmetric vibration an absorption band at  $\tilde{\nu} = 2062 \text{ cm}^{-1}$  was identified. The symmetric vibration was located at  $\tilde{\nu} = 2108 \text{ cm}^{-1}$ . The calculations were run using the Gaussian 09 (Revision D.01) program package<sup>[1]</sup> and the B3LYP functional. Rhodium<sup>[2]</sup> and Germanium<sup>[3]</sup> were described with RECPs and the associated cc-pVDZ basis sets. For all other atoms cc-pVDZ basis sets were used. The calculated structure was identified as a minimum (no negative eigenvalues). The resulting energy was corrected for zero-point energy. Cartesian coordinates for the optimized structure are given below.

Optimized cartesian coordinates for complex $[\text{Rh}(\text{GePh}_3)(\text{H})_2(\text{PEt}_3)_3]$ ( <b>2</b> ), energies are corrected for zero-point energy and given in Hartree:			
Energy: -2837.441091			
Rh	0.83605	-0.16250	0.07044
Ge	-1.67008	-0.28076	0.14399
H	0.51502	-0.70754	1.51329
H	0.36774	-1.58080	-0.44905
P	1.04067	0.43960	-2.32078
P	1.17756	1.99005	1.23067
P	2.89914	-1.36080	0.49682
C	-2.38156	-1.67647	1.42357
C	-1.59006	-2.33645	2.37685
H	-0.52541	-2.09885	2.44057
C	-2.12709	-3.29871	3.24232
H	-1.48162	-3.79440	3.97308
C	-3.48258	-3.62678	3.17051
H	-3.90648	-4.37776	3.84225
C	-4.29178	-2.98705	2.22548
H	-5.35399	-3.23745	2.15491
C	-3.74509	-2.02923	1.36583
H	-4.39794	-1.55028	0.63095
C	-2.59563	-0.92982	-1.53680
C	-2.39388	-2.26367	-1.94284
H	-1.74122	-2.91309	-1.35143
C	-3.01746	-2.78904	-3.07867
H	-2.84633	-3.83167	-3.36112
C	-3.86296	-1.98390	-3.85062
H	-4.35194	-2.38952	-4.74001
C	-4.08370	-0.65993	-3.46484
H	-4.75267	-0.02321	-4.05078
C	-3.46100	-0.14505	-2.31910
H	-3.67587	0.88574	-2.02722
C	-2.76417	1.35091	0.65248
C	-2.75686	2.51879	-0.13595
H	-2.17127	2.54792	-1.05815
C	-3.48536	3.65926	0.22259
H	-3.46160	4.54457	-0.41924
C	-4.24095	3.66660	1.39878
H	-4.80902	4.55510	1.68571
C	-4.26277	2.52231	2.20078
H	-4.85122	2.51209	3.12262
C	-3.53749	1.38354	1.82897
H	-3.57803	0.50269	2.47360
C	-0.09968	1.80463	-2.93556
H	-1.11224	1.43165	-2.71517
H	0.06245	2.66659	-2.27190
C	-0.01605	2.24697	-4.40079
H	0.96911	2.66760	-4.65835
H	-0.76518	3.03160	-4.59926
H	-0.22309	1.42138	-5.09867
C	0.56293	-0.92108	-3.51975
H	-0.51156	-1.09730	-3.36412
H	0.68331	-0.52218	-4.54066
C	1.32490	-2.23999	-3.38737
H	2.41074	-2.11625	-3.53752
H	0.97154	-2.96143	-4.14234
H	1.16298	-2.68789	-2.39627
C	2.67598	0.93395	-3.11208
H	3.36012	0.08590	-2.95927
H	2.50770	1.00172	-4.19992
C	3.31760	2.22306	-2.59859
H	2.68423	3.10306	-2.79715
H	4.28696	2.40189	-3.09333
H	3.49948	2.18152	-1.51470
C	0.00184	2.32386	2.65457
H	0.26598	3.30955	3.07202

H	-0.99793	2.41979	2.20672
C	-0.03016	1.28261	3.77466
H	-0.33419	0.29480	3.39965
H	-0.75745	1.58394	4.54633
H	0.94751	1.17480	4.27248
C	2.79247	2.33422	2.13618
H	2.63701	3.22225	2.77184
H	2.93254	1.48672	2.82482
C	4.03997	2.52379	1.27268
H	4.22370	1.65558	0.62195
H	4.93433	2.66114	1.90325
H	3.95917	3.41078	0.62452
C	0.94659	3.57190	0.24115
H	1.62594	3.49152	-0.62176
H	-0.07560	3.49520	-0.16161
C	1.13364	4.92638	0.93375
H	0.41718	5.07478	1.75577
H	0.97121	5.74481	0.21243
H	2.14848	5.05283	1.34340
C	2.53278	-3.19937	0.37350

H	1.65665	-3.34746	1.02497
H	2.15592	-3.34468	-0.65058
C	3.62213	-4.22907	0.68763
H	4.45213	-4.18792	-0.03429
H	3.20082	-5.24711	0.63788
H	4.04557	-4.10385	1.69698
C	3.68927	-1.25634	2.19870
H	4.56764	-1.92064	2.20702
H	4.07794	-0.23134	2.30736
C	2.76814	-1.60340	3.37064
H	1.88876	-0.94547	3.40600
H	3.30959	-1.50431	4.32609
H	2.40150	-2.64050	3.30784
C	4.40287	-1.13651	-0.62849
H	4.14658	-1.68470	-1.55156
H	4.40296	-0.07137	-0.90533
C	5.80626	-1.52477	-0.14497
H	6.12621	-0.91284	0.71267
H	6.54031	-1.36032	-0.95187
H	5.87790	-2.58013	0.15407

DFT-derived structures and energies for compounds 6a-6d:



**Figure 2.** DFT-optimized structures of complex  $[\text{Rh}(\text{GePh}_3)(\text{H})(\text{CH}_3)(\text{PET}_3)_2]$  (**6 a-d**) and their energies. The hydrogen atoms of the germyl ligand as well as of the phosphine ligands have been omitted for clarity.

Computational details for compounds **6a-6d** are given in the main text.

Optimized cartesian coordinates for complex [Rh(GePh<sub>3</sub>)(H)(CH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (**6a**), energies are corrected for zero-point energy and given in Hartree:

Energy: -2297.913066

Rh	1.07791	1.10933	0.18155
C	2.46639	2.37089	1.16357
H	2.69219	1.83484	2.09188
H	2.03749	3.33338	1.43157
H	3.40820	2.56411	0.65292
H	1.78175	1.66832	-1.03571
Ge	-0.87210	-0.68670	-0.07134
C	-1.11869	-1.43343	1.78563
C	-0.60643	-2.28882	-1.26162
C	-2.80844	-0.23422	-0.45973
C	-0.46591	-0.82535	2.87267
C	-1.99562	-2.49628	2.08159
C	-0.65998	-1.25406	4.19237
C	-1.52214	-2.32121	4.45490
C	-2.19106	-2.94097	3.39335
C	-0.41347	-3.59579	-0.77544
C	-0.33854	-3.18831	-3.53117
C	-0.15531	-4.47792	-3.02180
C	-0.18869	-4.67568	-1.63904
C	-0.55106	-2.11456	-2.66016
C	-3.63623	0.23853	0.57862
C	-3.39129	-0.34277	-1.73696
C	-4.72517	0.01302	-1.97054
C	-4.97050	0.59747	0.35458
C	-5.52139	0.49057	-0.92571
H	-2.87573	-3.77063	3.58978
H	-0.13875	-0.75382	5.01313
H	-1.67789	-2.66472	5.48061
H	-2.54995	-2.98102	1.27355
H	0.21136	0.01815	2.69066
H	-0.43767	-3.78399	0.30039
H	-0.04255	-5.67794	-1.22654
H	-0.30928	-3.01622	-4.61067
H	0.01502	-5.31982	-3.69735
H	-0.65678	-1.11245	-3.08673
H	-5.14511	-0.09061	-2.97502
H	-5.58370	0.95406	1.18702
H	-6.56330	0.76721	-1.10515
H	-2.80487	-0.72667	-2.57416
H	-3.23990	0.31048	1.59526
P	2.75269	-0.56972	0.02502
P	-0.35904	2.92191	-0.16897
C	4.48875	0.07124	0.20511
C	2.81820	-1.43502	-1.60870
C	5.64057	-0.92422	0.02336
C	2.99186	-0.51874	-2.82328
C	0.44583	4.59443	-0.33812
C	-1.44763	2.84656	-1.66742
C	2.71878	-2.00740	1.20013
C	3.08799	-1.66117	2.64686
C	1.58059	4.73073	-1.35704
C	-0.79146	2.37434	-2.96863
C	-1.61628	3.31501	1.13844

C	-1.06112	3.41722	2.56279
H	4.54837	0.54316	1.19679
H	4.58050	0.89789	-0.51671
H	1.88050	-1.99966	-1.69573
H	3.63296	-2.17611	-1.56537
H	6.60657	-0.41944	0.18811
H	5.66677	-1.35204	-0.99057
H	5.58516	-1.76119	0.73698
H	2.17184	0.21264	-2.88978
H	2.98998	-1.11304	-3.75082
H	3.94061	0.04190	-2.79136
H	3.39164	-2.78872	0.80947
H	1.69826	-2.41721	1.15550
H	4.13359	-1.32622	2.73649
H	2.96521	-2.54345	3.29455
H	2.44356	-0.86695	3.05250
H	0.81435	4.86993	0.66218
H	-0.36749	5.30285	-0.57211
H	-2.26261	2.15753	-1.40165
H	-1.89930	3.84531	-1.79718
H	-0.31412	1.39141	-2.83234
H	-0.02143	3.07203	-3.33172
H	-1.55086	2.27644	-3.76091
H	2.38663	4.00951	-1.15749
H	2.01363	5.74328	-1.31306
H	1.23069	4.56865	-2.38772
H	-2.37786	2.52287	1.08400
H	-2.11602	4.25554	0.84800
H	-0.60908	2.46645	2.88524
H	-1.86809	3.65908	3.27274
H	-0.29352	4.20178	2.65736

Optimized cartesian coordinates for complex [Rh(GePh<sub>3</sub>)(H)(CH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (**6b**), energies are corrected for zero-point energy and given in Hartree:

Energy: -2297.909020

Rh	1.12679	1.03586	-0.06979
C	1.66316	1.42499	-2.02878
H	2.31170	2.05907	0.13866
H	1.10344	0.68703	-2.60146
H	2.72816	1.30361	-2.21044
H	1.37712	2.42382	-2.33857
Ge	-0.90357	-0.70022	-0.02425
C	-1.33575	-1.48577	1.78359
C	-0.64251	-2.32296	-1.19349
C	-2.76200	-0.10406	-0.56113
C	-0.64181	-1.08324	2.93773
C	-2.37630	-2.42104	1.95976
C	-0.95220	-1.58989	4.20707
C	-1.97927	-2.52497	4.35083
C	-2.69312	-2.93788	3.22012
C	-0.60102	-3.63773	-0.68994
C	-0.22360	-3.26016	-3.42478
C	-0.19394	-4.55579	-2.89968
C	-0.37900	-4.73895	-1.52642
C	-0.43569	-2.16563	-2.57911
C	-3.66641	0.37184	0.40981
C	-3.19766	-0.08079	-1.89983

C	-4.46321	0.40042	-2.25517
C	-4.93356	0.85696	0.06460
C	-5.33735	0.87746	-1.27372
H	-3.50515	-3.66320	3.32162
H	-0.39218	-1.25058	5.08299
H	-2.22735	-2.92589	5.33681
H	-2.95997	-2.74813	1.09513
H	0.16039	-0.34543	2.85099
H	-0.74635	-3.81283	0.37847
H	-0.35518	-5.74634	-1.10124
H	-0.07599	-3.10001	-4.49650
H	-0.02654	-5.41414	-3.55511
H	-0.43059	-1.16276	-3.01664
H	-4.76958	0.39612	-3.30508
H	-5.61063	1.21257	0.84654
H	-6.32672	1.25201	-1.54807
H	-2.54704	-0.46021	-2.69094
H	-3.38751	0.34690	1.46702
P	2.84373	-0.57360	0.13868
P	-0.22052	2.95007	0.09040
C	4.52914	0.19410	-0.03108
C	2.95798	-2.08737	-0.92482
C	5.75405	-0.70281	0.17762
C	3.26039	-1.83769	-2.40625
C	0.69111	4.57235	0.13033
C	-1.65181	3.28512	-1.04394
C	2.89213	-1.33814	1.82852
C	3.11720	-0.34859	2.97732
C	1.59335	4.92266	-1.05617
C	-1.41143	3.15839	-2.55106
C	-1.10290	3.04550	1.72206
C	-0.20985	2.94526	2.96284
H	4.53666	1.03750	0.67655
H	4.55514	0.65653	-1.03097
H	1.99518	-2.60908	-0.82194
H	3.72863	-2.74229	-0.48393
H	6.68027	-0.11537	0.06830
H	5.80093	-1.52379	-0.55468
H	5.77131	-1.15252	1.18314
H	2.47078	-1.24350	-2.88624
H	3.31991	-2.79731	-2.94302
H	4.21875	-1.31355	-2.55327
H	3.67404	-2.11539	1.83637
H	1.92881	-1.85626	1.95554
H	4.11927	0.10688	2.93618
H	3.02441	-0.85903	3.94899
H	2.38380	0.47305	2.95995
H	1.30349	4.53677	1.04581
H	-0.06672	5.36115	0.28261
H	-2.43270	2.57101	-0.74283
H	-2.02402	4.29443	-0.79390
H	-1.07510	2.14585	-2.81631
H	-0.66406	3.87560	-2.92428
H	-2.35145	3.34641	-3.09359
H	2.37799	4.16422	-1.19501
H	2.08906	5.89131	-0.88087
H	1.03024	5.00957	-1.99799
H	-1.83809	2.22643	1.71652
H	-1.67740	3.98803	1.73749

H	0.38104	2.01581	2.96076
H	-0.82297	2.94397	3.87798
H	0.49426	3.78865	3.03827

Optimized cartesian coordinates for complex  
[Rh(GePh<sub>3</sub>)(H)(CH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (6c), energies are corrected  
for zero-point energy and given in Hartree:

Energy: -2297.907361

Rh	0.17447	-1.56684	0.09110
Ge	-0.14297	1.06031	-0.04927
C	-0.07086	1.51516	1.91586
C	-1.85616	2.01300	-0.56464
C	1.21871	2.26958	-0.91957
C	-2.12100	2.42288	-1.88639
C	-3.33094	3.02712	-2.24407
C	-4.32395	3.23916	-1.28256
C	-4.08524	2.84860	0.03767
C	-2.86895	2.24763	0.38639
C	2.09220	3.10537	-0.19719
C	3.02134	3.93275	-0.84139
C	3.10261	3.95027	-2.23629
C	2.25335	3.12325	-2.97805
C	1.33574	2.29400	-2.32428
C	-0.12485	2.82475	2.43261
C	-0.11527	3.07090	3.81005
C	-0.06276	2.00573	4.71596
C	-0.02337	0.69519	4.23306
C	-0.02660	0.46493	2.85128
H	-1.36738	2.27842	-2.66334
H	-3.49657	3.33742	-3.27959
H	-5.27015	3.71123	-1.55853
H	-4.84516	3.01961	0.80548
H	-2.70300	1.97574	1.43182
H	2.04795	3.12318	0.89428
H	3.68070	4.57171	-0.24716
H	3.82212	4.59968	-2.74101
H	2.30749	3.12063	-4.07026
H	0.69909	1.64523	-2.93368
H	-0.18818	3.67312	1.74588
H	-0.15528	4.09949	4.17900
H	-0.05864	2.19649	5.79201
H	0.00899	-0.14713	4.92932
H	-0.00367	-0.57696	2.50005
P	-2.11663	-1.98149	-0.19244
P	2.52290	-1.39091	-0.17320
C	-2.60911	-3.76104	-0.38109
C	-2.82616	-1.19214	-1.71582
C	-4.14371	-1.71352	-2.30428
C	-1.90602	-4.50748	-1.51931
C	-3.13970	-1.44257	1.25980
C	-4.66718	-1.57268	1.22346
C	3.51269	-0.26449	0.91816
C	2.92248	-0.87449	-1.91917
C	3.54009	-0.68014	2.39358
C	4.21444	-0.09695	-2.19658
C	3.41662	-3.01343	-0.01144
C	4.92052	-3.05590	-0.30452
H	-2.90876	-0.12234	-1.47869

H	-2.02410	-1.26255	-2.46818	C	0.41081	1.21915	2.85387
H	-2.40781	-4.25903	0.57952	H	-1.87964	2.04824	-2.57189
H	-3.70074	-3.78925	-0.52288	H	-4.21459	2.71277	-2.97663
H	-2.72610	-2.01804	2.10638	H	-5.83918	2.84662	-1.08288
H	-2.85829	-0.39543	1.44448	H	-5.06196	2.32840	1.23577
H	-4.97659	-1.66293	-1.58841	H	-2.71897	1.67694	1.64647
H	-4.06638	-2.75411	-2.65537	H	1.80322	3.50628	0.09321
H	-4.42455	-1.09735	-3.17413	H	3.14843	4.75709	-1.55252
H	-0.81846	-4.54002	-1.36177	H	2.99890	4.21073	-3.98488
H	-2.08804	-4.03124	-2.49614	H	1.47844	2.37632	-4.73869
H	-2.27228	-5.54469	-1.58489	H	0.15084	1.10817	-3.09684
H	-5.00043	-2.59788	0.99783	H	-0.44565	3.99265	1.08904
H	-5.11238	-0.89511	0.47991	H	-0.14205	5.02596	3.31160
H	-5.08878	-1.30013	2.20483	H	0.50266	3.62543	5.27606
H	3.07417	0.73834	0.81012	H	0.83807	1.16883	4.97747
H	4.53864	-0.20179	0.52378	H	0.55342	0.13889	2.74874
H	2.89553	-1.81187	-2.50169	P	-1.90854	-2.20226	0.04179
H	2.06274	-0.28097	-2.25448	P	2.67007	-1.31111	0.08600
H	3.21918	-3.38020	1.00702	C	-2.13028	-4.04420	-0.00038
H	2.88011	-3.70681	-0.67828	C	-3.12315	-1.55417	-1.20301
H	5.11834	-0.63957	-1.88236	C	-4.40895	-2.34149	-1.48588
H	4.20923	0.88236	-1.69647	C	-1.57581	-4.74276	-1.24565
H	4.30409	0.09542	-3.27819	C	-2.57884	-1.76996	1.71941
H	2.52764	-0.74226	2.81918	C	-4.02083	-2.14080	2.08553
H	4.09882	0.06157	2.98631	C	3.25851	-0.98567	1.81416
H	4.03250	-1.65496	2.53951	C	3.57612	-0.07166	-0.96642
H	5.49219	-2.36875	0.33907	C	2.71296	-1.97220	2.85368
H	5.14488	-2.79979	-1.35086	C	4.88579	0.53228	-0.44308
H	5.31178	-4.07095	-0.12558	C	3.47210	-2.92768	-0.35924
C	0.41921	-3.47195	0.99107	C	5.00055	-3.03057	-0.36005
H	-0.52011	-3.84463	1.39825	H	-3.35602	-0.53059	-0.87426
H	1.10049	-3.30876	1.83128	H	-2.55401	-1.43119	-2.13785
H	0.84314	-4.26237	0.37232	H	-1.61294	-4.41986	0.89787
H	0.28290	-2.31884	-1.21788	H	-3.19996	-4.27687	0.12331

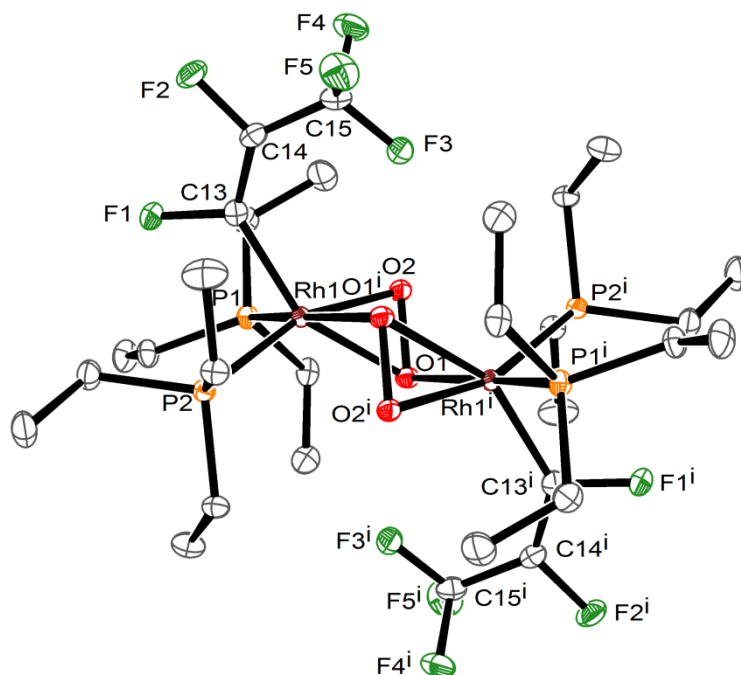
Optimized cartesian coordinates for compound [Rh(GePh<sub>3</sub>)(H)(CH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (**6d**), energies are corrected for zero-point energy and given in Hartree:

Energy: -2297.906895

Rh	0.32195	-1.48146	-0.05888
Ge	-0.22901	1.10195	-0.06673
C	0.06044	1.98307	1.72638
C	-2.10544	1.77049	-0.43219
C	0.84431	2.21470	-1.36079
C	-2.56755	2.08628	-1.72423
C	-3.89331	2.46879	-1.96000
C	-4.80374	2.54739	-0.90166
C	-4.36779	2.25287	0.39380
C	-3.03868	1.87418	0.61911
C	1.71567	3.24783	-0.96462
C	2.48432	3.95844	-1.89520
C	2.40264	3.65465	-3.25711
C	1.55020	2.62895	-3.67706
C	0.79121	1.91982	-2.73935
C	-0.14227	3.36322	1.92990
C	0.01985	3.95149	3.18846
C	0.37926	3.16818	4.29107
C	0.56929	1.79489	4.12195

H	-1.87964	2.04824	-2.57189
H	-4.21459	2.71277	-2.97663
H	-5.83918	2.84662	-1.08288
H	-5.06196	2.32840	1.23577
H	-2.71897	1.67694	1.64647
H	1.80322	3.50628	0.09321
H	3.14843	4.75709	-1.55252
H	2.99890	4.21073	-3.98488
H	1.47844	2.37632	-4.73869
H	0.15084	1.10817	-3.09684
H	-0.44565	3.99265	1.08904
H	-0.14205	5.02596	3.31160
H	0.50266	3.62543	5.27606
H	0.83807	1.16883	4.97747
H	0.55342	0.13889	2.74874
P	-1.90854	-2.20226	0.04179
P	2.67007	-1.31111	0.08600
C	-2.13028	-4.04420	-0.00038
C	-3.12315	-1.55417	-1.20301
C	-4.40895	-2.34149	-1.48588
C	-1.57581	-4.74276	-1.24565
C	-2.57884	-1.76996	1.71941
C	-4.02083	-2.14080	2.08553
C	3.25851	-0.98567	1.81416
C	3.57612	-0.07166	-0.96642
C	2.71296	-1.97220	2.85368
C	4.88579	0.53228	-0.44308
C	3.47210	-2.92768	-0.35924
C	5.00055	-3.03057	-0.36005
H	-3.35602	-0.53059	-0.87426
H	-2.55401	-1.43119	-2.13785
H	-1.61294	-4.41986	0.89787
H	-3.19996	-4.27687	0.12331
H	-1.87431	-2.23717	2.42991
H	-2.43657	-0.68368	1.81964
H	-5.02825	-2.47819	-0.58739
H	-4.20501	-3.33833	-1.90667
H	-5.01928	-1.79478	-2.22303
H	-0.49142	-4.58218	-1.33392
H	-2.04844	-4.37695	-2.17163
H	-1.75722	-5.82822	-1.19002
H	-4.21920	-3.21902	1.98370
H	-4.74734	-1.59729	1.46336
H	-4.22233	-1.86855	3.13447
H	2.94128	0.03997	2.05969
H	4.35959	-0.98997	1.82805
H	3.74193	-0.57451	-1.93461
H	2.86219	0.73751	-1.16742
H	3.02957	-3.66943	0.32374
H	3.07308	-3.17640	-1.35607
H	5.65666	-0.22322	-0.22991
H	4.72274	1.11684	0.47537
H	5.29699	1.22456	-1.19543
H	1.61118	-1.98992	2.86256
H	3.05179	-1.69356	3.86417
H	3.05370	-3.00185	2.66105
H	5.43619	-2.78929	0.62269
H	5.45993	-2.36280	-1.10474

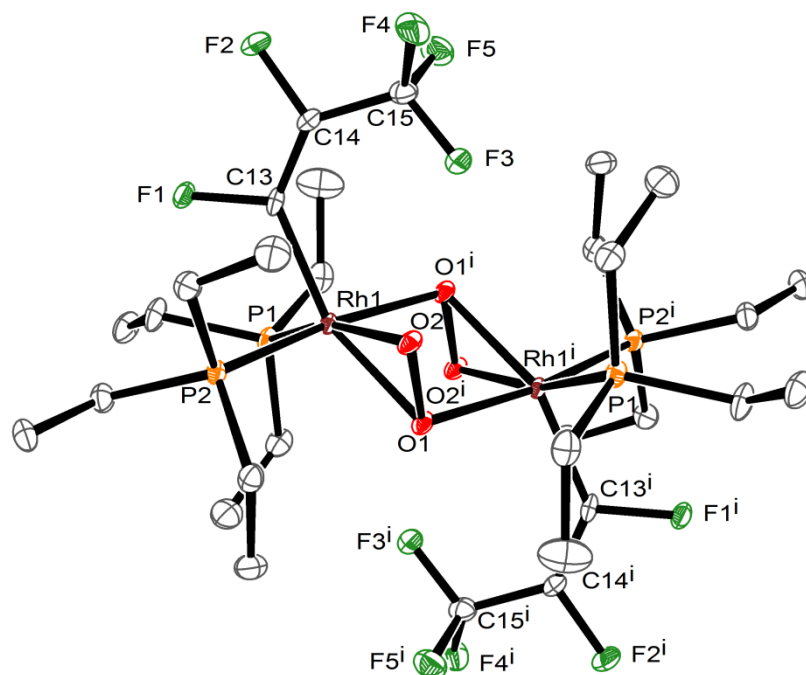
H	5.31123	-4.05848	-0.60950
C	0.49185	-1.83588	-2.08571
H	-0.49068	-1.76164	-2.54724
H	0.91484	-2.81353	-2.30323
H	1.13127	-1.05458	-2.49213
H	0.63932	-3.03399	0.09528



**Figure 3.** An ORTEP diagram of **14a**. Ellipsoids are drawn at the 50% probability level. C–H hydrogen atoms were omitted for clarity.

The molecular structure of **14b** in the solid state was determined by X-ray crystallography (Figure 4). Yellow crystals (needles) were obtained from toluene/*n*-hexane solution at 243 K. Selected bond lengths and angles are summarized in Table 1.

The molecular structure in the solid state of **14a** and **14b** differs in the coordination geometry at the rhodium metal center as well as in the conformation of the ethyl groups of the phosphine ligands. In the case of **14a** the peroxide unit is directed towards the back whereas in **14b** it is directed towards the front.



**Figure 4.** An ORTEP diagram of **14b**. Ellipsoids are drawn at the 50% probability level. The ethyl groups of the phosphine ligands atoms were omitted for clarity.

**Table 1.** Selected bond lengths [Å] and angles [°] in  $[\text{Rh}\{(E)\text{-CF}=\text{CF}(\text{CF}_3)(\mu\text{-}\kappa^1\text{:}\eta^2\text{-O}_2)(\text{PEt}_3)_2\}]_2$  (**14b**).

Lengths [Å]			
Rh1–O1	2.1556(14)	O2–O2 <sup>i</sup>	3.558(2)
Rh1 <sup>i</sup> –O1	2.0957(15)	O1–O2 <sup>i</sup>	2.784(2)
Rh1–O2	2.0031(15)	C13–C14	1.323(3)
Rh1–P1	2.3497(6)	C13–F1	1.392(2)
Rh1–P2	2.2868(6)	C14–F2	1.380(3)
Rh1–C13	1.991(2)	Rh1–O <sub>middle</sub>	1.9480(13)
O1–O2	1.463(2)	Rh1 <sup>i</sup> –O <sub>middle</sub>	2.3598(13)
O1–O1 <sup>i</sup>	2.668(2)		
Angles [°]			
O1–Rh1–P1	121.00(4)	O2–O1–Rh1	63.90(8)
O1–Rh1–P2	90.95(4)	O2 <sup>i</sup> –O1 <sup>i</sup> –Rh1	101.89(10)
O2–Rh1–P1	161.65(5)	O2–Rh1–C13	108.41(8)
O2–Rh1–P2	82.02(5)	C13–Rh1–O1	149.00(8)
P2–Rh1–P1	104.81(2)	C13–Rh1–O1 <sup>i</sup>	98.49(8)
O2–Rh1–O1	40.99(6)	C13–Rh1–P1	89.03(7)
O1–Rh1–O1 <sup>i</sup>	77.72(6)	C13–Rh1–P2	88.14(7)
O2–Rh1–O1 <sup>i</sup>	85.51(6)	Rh1–O1–Rh1 <sup>i</sup>	102.28(6)
O1 <sup>i</sup> –Rh1–P1	86.32(4)	O1–O2–Rh1	75.11(9)
O1 <sup>i</sup> –Rh1–P2	167.22(4)		

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