

Supporting Information

Chemistry of 11-vertex rhodathiaboranes: reactions with monodentate phosphines

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1. NMR Data for [8,8-(PPh₃)₂-nido-8,7-RhSB₉H₁₀] (1)

Table 1 gathers the published NMR data (George Ferguson *et al. J. Chem.Soc., Chem. Commun.* **1990**, 891) together with new DFT-calculated data.

Table 1 ¹¹B, ¹H-¹¹B and ³¹P-¹H NMR data for compound **1** in CD₂Cl₂ with the corresponding DFT-calculated chemical shifts

Assignment ^a	Cluster data		$\delta(^1\text{H})$ (ppm)
	$\delta(^{11}\text{B})$ (ppm)		
	measured	calculated	
3	16.3	26.7	4.14
9	12.6	22.5	3.59
6	6.0	11.7	3.26
11	4.5	10.2	2.32
4	2.5	5.9	2.38
5	-9.3	-12.3	1.78
1	-18.6	-12.3	1.56
10	-21.1	-16.0	1.24
2	-27.5	-29.4	1.28
μ (9, 10)			-1.32

^a Based on ¹H-¹¹B_{sel} experiments, fluxional process and DFT calculations.

Assignment ^a	PPh ₃ data in CD ₂ Cl ₂ solution at 223 K			
	$\delta(^{31}\text{P})$ (ppm) ^b		¹ J(¹⁰³ Rh- ³¹ P)	² J(³¹ P- ³¹ P) (Hz)
	measured	calcd.	(Hz) ^c	
P(1)	43.0	64.9	160	35.5
P(2)	20.3	27.6	128	

^a Based on DFT-calculations. ^b Measured at 273 K. ^c The signals are broad, precluding an accurate measurement; ²J(³¹P-³¹P) coupling constants not observed. ^d Measured at 300 K

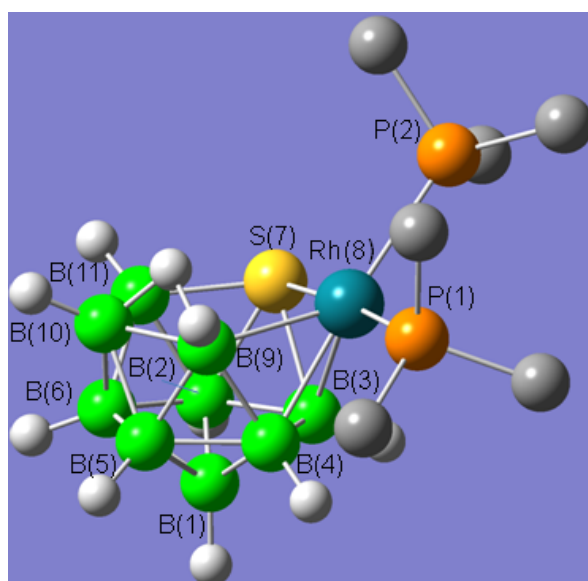


Figure S1 DFT-calculated molecular structure of compound **1** with the labeling used in the main manuscript.

2. NMR Data for [8,8-(PMe₃)(PPh₃)-*nido*-8,7-RhSB₉H₁₀] (6)

Table 2 ³¹P-¹H NMR data for compound 6 in CD₂Cl₂ with the corresponding DFT-calculated chemical shifts

Assignment ^a	calcd. $\delta(^{31}\text{P})$	Assignment ^a	calcd. $\delta(^{31}\text{P})$	measured $\delta(^{31}\text{P})$
PPh ₃ trans to B(4)	27.3	PPh ₃ trans to S(7)	55.6	25.1
PMe ₃ trans to S(7)	16.6	PMe ₃ trans to B(4)	-39.3	5.1

^a Based on DFT calculations.

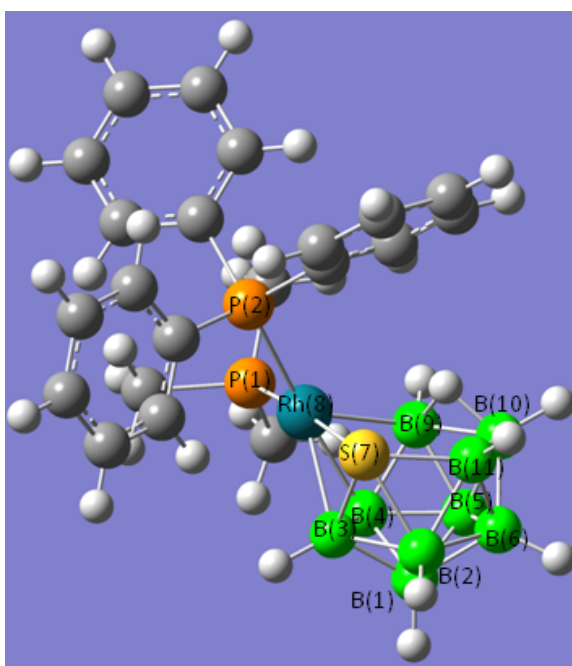


Figure S2 DFT-calculated molecular structure of compound 6 with the labeling used in the main manuscript.

3. $^{31}\text{P}\{-^1\text{H}\}$ NMR for $[\text{8,8-(PMe}_3)_3\text{-nido-8,7-RhSB}_9\text{H}_{10}]$ (8)

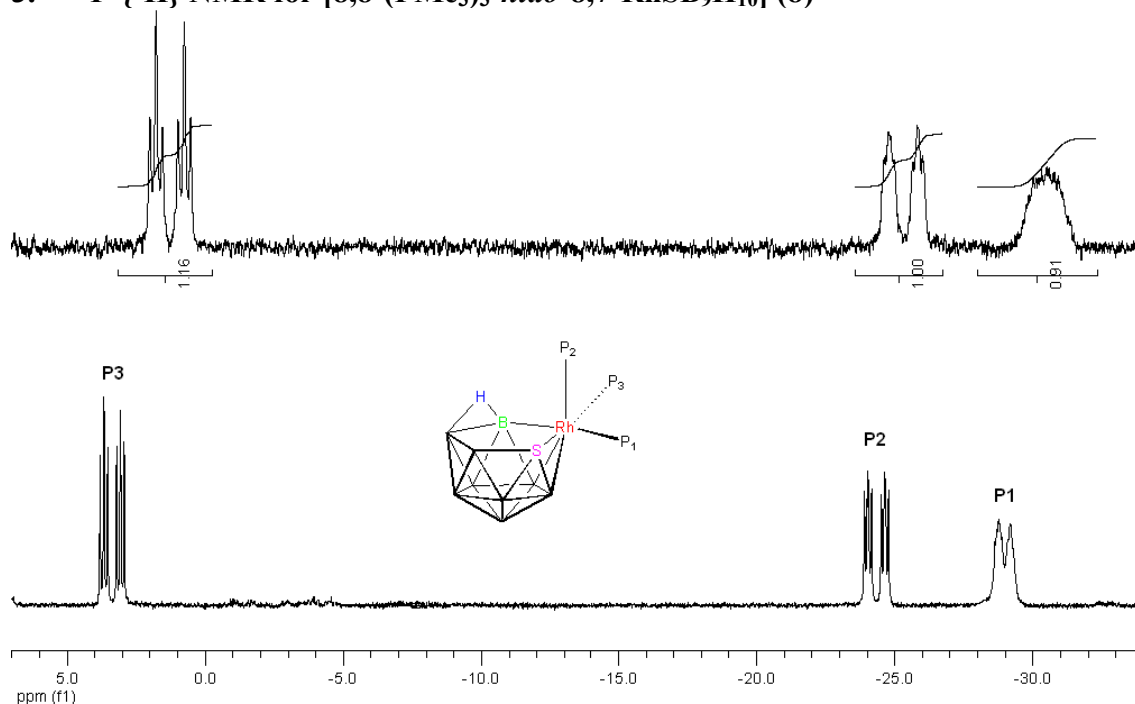


Figure S3 $^{31}\text{P}\{-^1\text{H}\}$ spectrum of compound 6 at room temperature (upper trace) and at 223 K (lower trace).

4. NMR variable temperature studies

4.1. Reaction of 1 with PPh_2Me

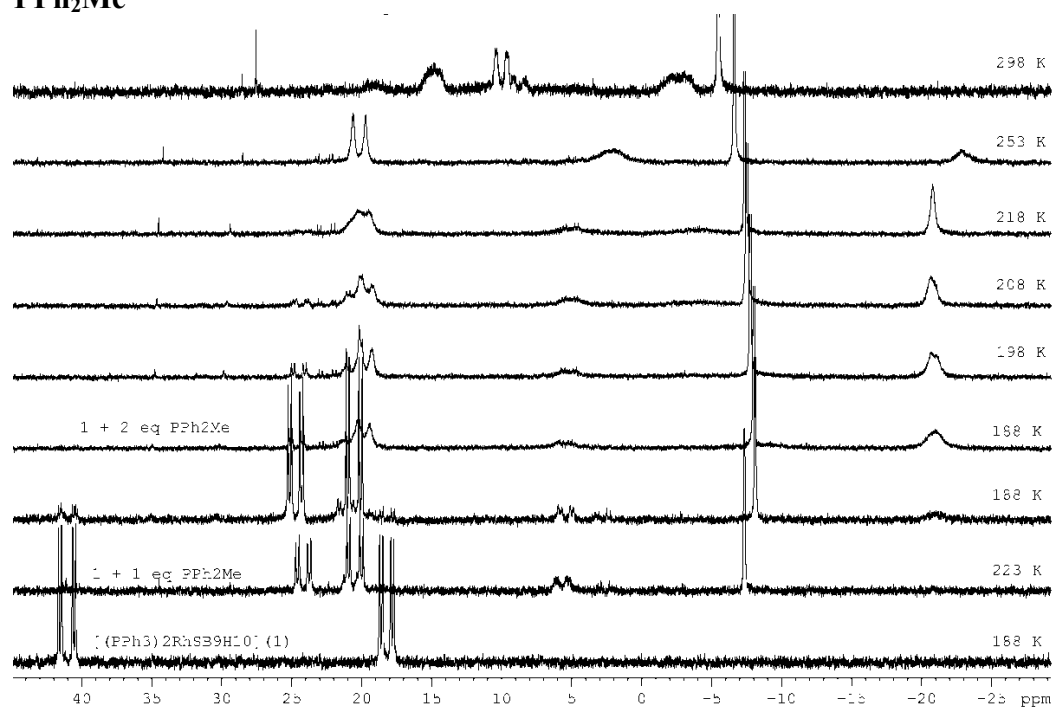


Figure S4 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **1** upon addition of PPh_2Me : the spectrum at the bottom corresponds to the starting material; the next two spectra were measured after the addition of 1 equivalent of PPh_2Me ; whereas the next five spectra were recorded after addition of another equivalent of phosphine. The spectrum at the top was measured after leaving the NMR tube at room temperature for 14 h.

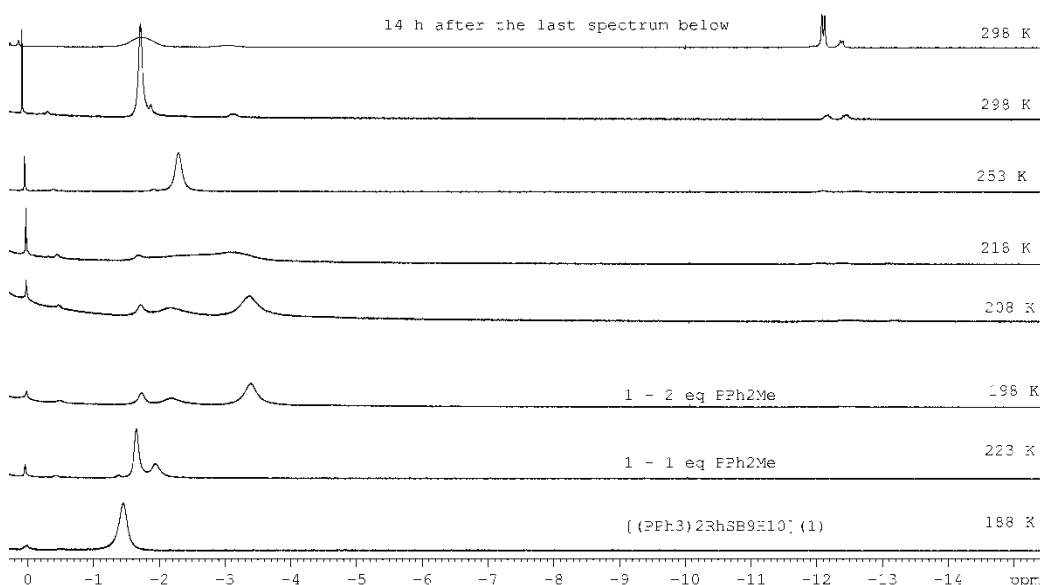


Figure S5 $^1\text{H}\{-^{11}\text{B}\}$ NMR spectra of **1** upon addition of PPh_2Me at different temperatures. Each spectrum has its corresponding $^{31}\text{P}\{-^1\text{H}\}$ spectrum above (Figure 3). The spectrum at the top was taken without boron-decoupling.

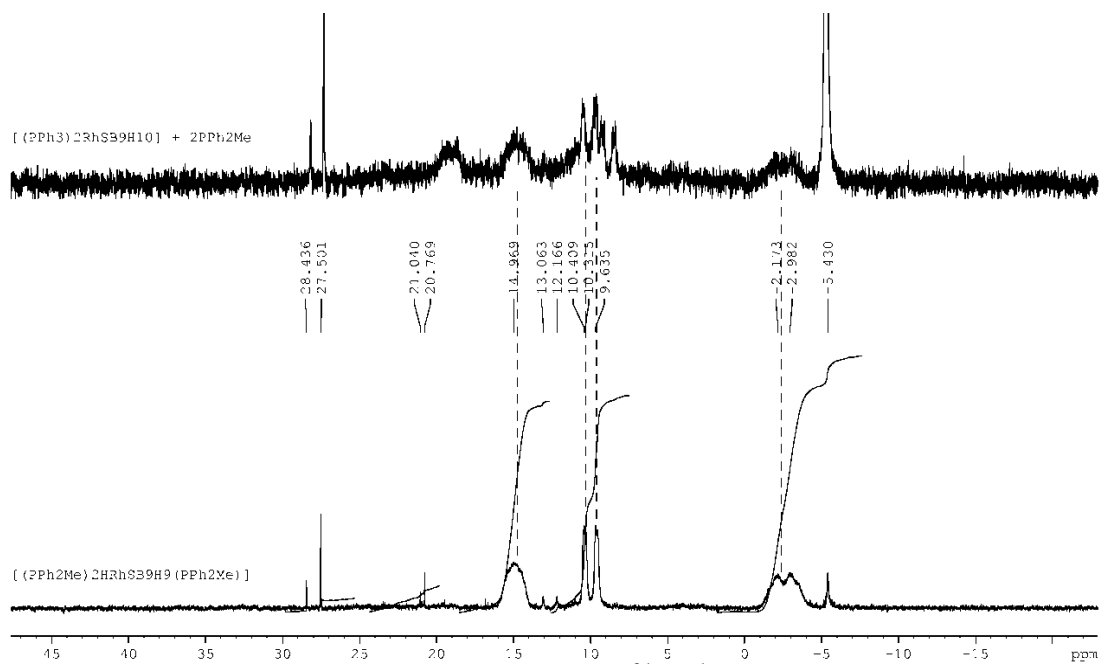


Figure S6 Comparison of the room temperature $^{31}\text{P}\{-^1\text{H}\}$ spectrum of **9** (lower trace) with that obtained from the treatment of **1** with 2 equivalents of PPh_2Me at low temperature (Figures S3 and S4), leaving the NMR tube at room temperature overnight (upper trace).

4.2. Variable temperature behaviour of **9** in the presence of PPh_3

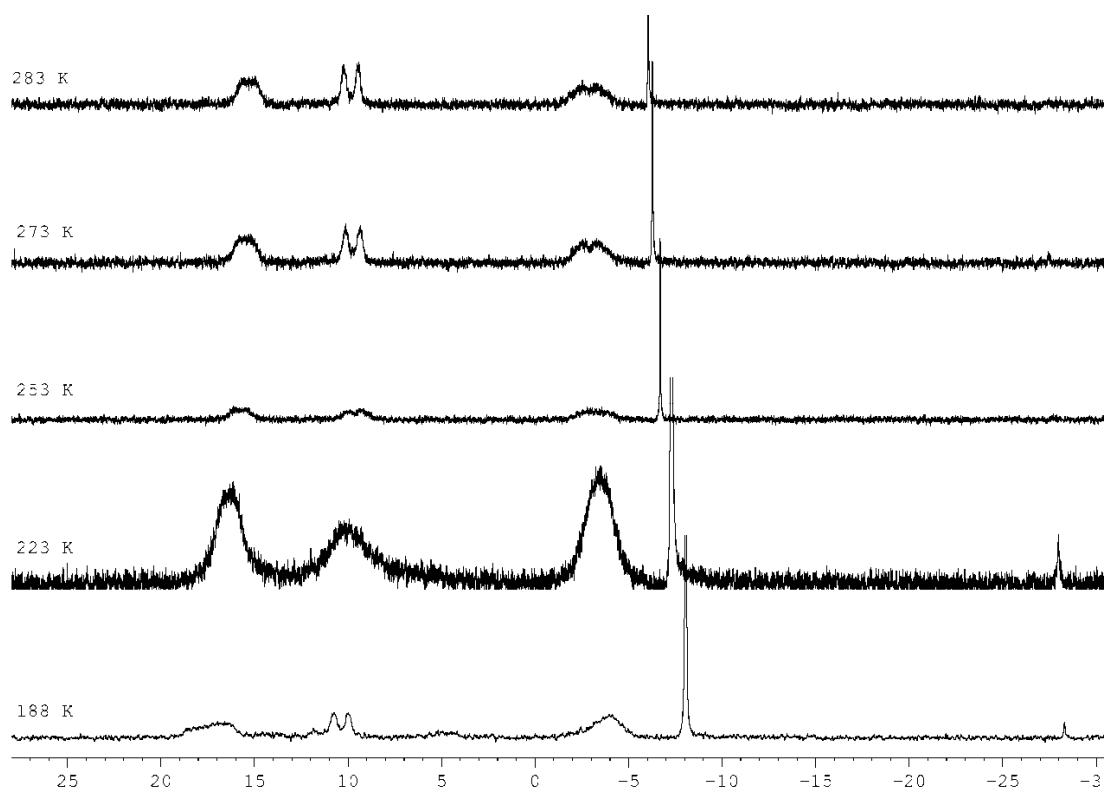


Figure S7 $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **9** in the presence of one equivalent of PPh_3 at different temperatures.

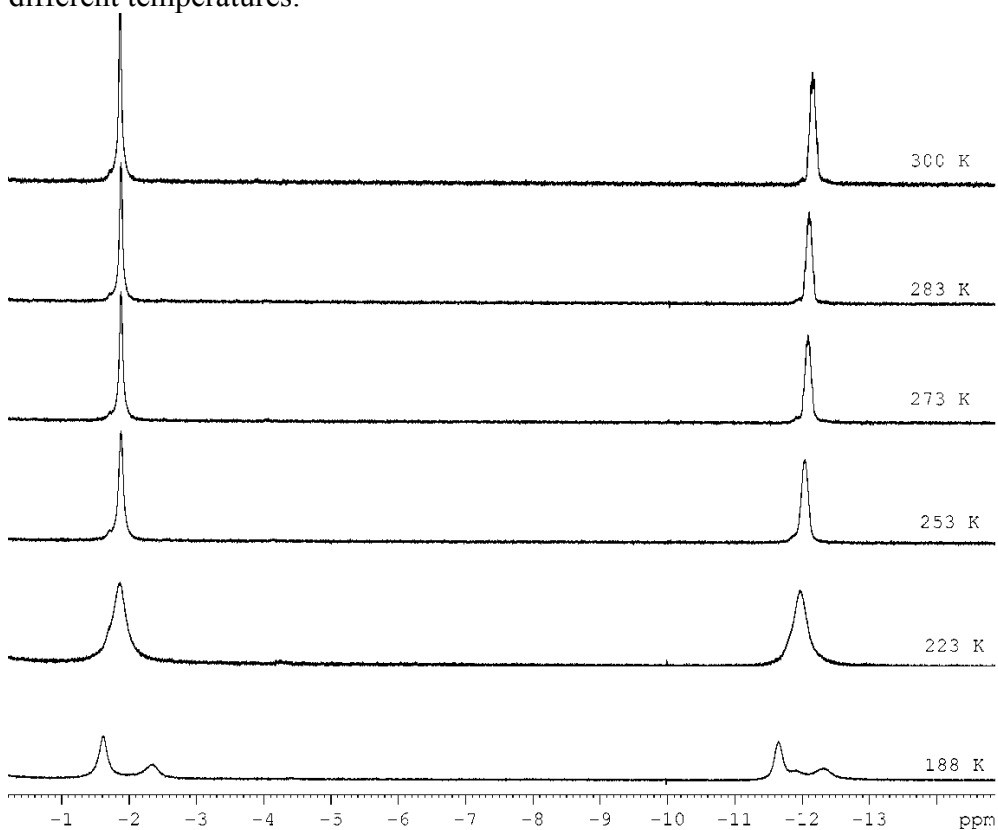


Figure S8 $^1\text{H}\{-^{11}\text{B}\}$ NMR spectra of **9** at different temperatures: each spectrum has its corresponding phosphorous-31 counterpart in Figure 6 above.

- 5. Tables of the optimized geometries (Cartesian coordinates, in Angstroms) for the calculated species. Energies (in Hartrees) in parenthesis.**

Table S1. [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (1) (-2810.14680578)

Rh	-1.1122937038	-0.2465649295	0.3058086942
B	-3.0625360597	2.3656109824	1.5200703037
B	-1.6712189659	1.5601582792	-0.8978979723
B	-2.4594362588	0.763611075	1.8606843499
B	-1.4871933114	1.900644686	0.8439140745
B	-4.5468618457	0.6446329716	-0.268844849
B	-3.4534027025	1.7756625203	-1.2954058447
B	-4.2770724472	1.0915118529	1.4940146367
B	-2.6105805439	2.8509444955	-0.1422189578
B	-4.269769013	2.2799401796	0.1867308559
S	-3.5150663274	-0.6048853217	0.7714985148
P	1.1759015474	0.264137915	-0.0422969342
P	-0.9311643051	-2.8069859139	0.1034341619
C	1.744861091	2.0040304937	-0.3291090439
C	1.9018124342	2.5106712771	-1.6274906862
C	1.9953828044	2.8530979913	0.7617341967
C	2.3055106897	3.8318099826	-1.8298470915
C	2.4024513171	4.1706764194	0.5566172406
C	2.5577515883	4.6646955915	-0.7400634823
C	1.8293976866	-0.5832485422	-1.5558259862
C	3.1657140145	-0.9803919164	-1.7119147943
C	0.9367555138	-0.784846801	-2.6211871519
C	3.5976200763	-1.5620885554	-2.9047917725
C	1.3705627813	-1.3631364532	-3.8164229301
C	2.7031769591	-1.7534854723	-3.9607159102
C	2.2466354443	-0.2466938524	1.3746838534
C	3.602758195	0.1163824615	1.4666407139
C	1.6757470856	-0.9766136744	2.4256416641
C	4.3689238297	-0.2746140901	2.5641874748
C	2.4403171153	-1.3607135483	3.5290583336
C	3.7900667202	-1.017289618	3.5966982202
H	-3.1254930459	3.1648299984	2.4014604429
H	-0.8866767745	1.749021114	-1.7739483377
H	-2.1631286799	0.3475034962	2.936721657
H	-0.5361952685	2.4334374318	1.3160726573
H	-5.557648129	0.1744502225	-0.6815527597
H	-3.8100141475	2.1399380287	-2.3727295205
H	-2.6719898823	0.7838996343	-1.4487837687
H	-5.1079871287	0.9088261679	2.321538438
H	-2.4045669212	3.9951556042	-0.4017273268
H	-5.1818749516	3.0340076926	0.0462900197
H	1.7145603279	1.8779009308	-2.4880538562
H	1.8751996222	2.4874171801	1.7758943225
H	2.4215933552	4.2063396154	-2.8432189731
H	2.5906996112	4.81239031	1.4129366245
H	2.8712473677	5.6929303191	-0.898826447
H	3.8722925158	-0.8554338114	-0.8994564179
H	-0.1027778481	-0.4924049105	-2.5103849189
H	4.6357066219	-1.867377969	-3.0073770289
H	0.663814522	-1.5125283604	-4.6278741468
H	3.0428295395	-2.2054503977	-4.8887749889
H	4.0549357832	0.7326280303	0.69606058
H	0.6205877654	-1.2260942008	2.3822814615
H	5.4151850662	0.0137153322	2.6194662844
H	1.9772849849	-1.9216116755	4.3361664567
H	4.3867231747	-1.3131869172	4.4553579642

C	0.6317559251	-3.790845065	0.3018564541
C	1.5508680483	-3.8908004057	-0.7563326254
C	0.9452748755	-4.4110728518	1.5222654074
C	2.7423782953	-4.599474859	-0.5981183001
H	1.335178319	-3.4293516097	-1.713563421
C	2.1416431796	-5.1125805744	1.6791449262
H	0.249845403	-4.3605683697	2.353100704
C	3.0439194594	-5.2112426412	0.6196987748
H	3.4347441207	-4.668698954	-1.4325540292
H	2.3614221666	-5.5892482347	2.6307616282
H	3.9725434137	-5.7625056641	0.7406908627
C	-2.0263549046	-3.6124912208	1.365352102
C	-2.1044333221	-3.0418591036	2.6460950497
C	-2.757432107	-4.7798459796	1.1014753646
C	-2.8771928826	-3.6353769983	3.6452696535
H	-1.5815461949	-2.1136640852	2.8591252574
C	-3.5390157669	-5.3663230603	2.0983753482
H	-2.7289774894	-5.2304975163	0.1152027631
C	-3.5970887507	-4.7997494861	3.3727887572
H	-2.9293233791	-3.1761287872	4.6284844326
H	-4.1061115106	-6.266034781	1.8750457467
H	-4.2088936492	-5.2565099974	4.1458816576
C	-1.5925998602	-3.3958156329	-1.5207374892
C	-2.4120352118	-2.5330475774	-2.2649420095
C	-1.3313361428	-4.6806874938	-2.0274853056
C	-2.9649228579	-2.9433173181	-3.4794898806
H	-2.6161989364	-1.5341583199	-1.8924746331
C	-1.8811787355	-5.0883487662	-3.2437470507
H	-0.6884511161	-5.3615120259	-1.4787313263
C	-2.6998832782	-4.2219335022	-3.9718049799
H	-3.5989918847	-2.2604625768	-4.0380403844
H	-1.667916395	-6.0846502309	-3.6219163877
H	-3.1260965104	-4.5416876323	-4.9188617571

Table S2. [8,8-(PPh₃)(PMe₃)-*nido*-8,7-RhSB₉H₁₀] (**6**) (-2234.97519525)

Rh	-1.3114727582	1.0343119015	1.1561150781
B	-2.160883652	4.4055474395	0.8561544345
B	-1.710615046	2.3657648156	2.888535961
B	-1.6434580431	2.9916266269	-0.0308375825
B	-2.6756996525	2.8078903819	1.43535945
B	0.5938647494	4.007340951	1.6468749636
B	-0.5092095639	3.7281399162	3.1477935276
B	-0.5136807417	4.4715827296	0.2459796472
B	-2.1848203519	4.0440197978	2.6071339235
B	-0.8152321682	4.9570971044	1.9163165078
S	0.341958742	2.6681806787	0.2835107929
P	-2.9939079005	-0.3626765386	1.9261635264
P	0.43316598	-0.7156173099	0.7804636388
C	0.3640484008	-2.4670078637	1.4013087428
C	-0.3381882913	-3.4406774257	0.6688325637
C	0.9359334736	-2.8393788965	2.6280461165
C	-0.4691655469	-4.7432764005	1.1515583475
C	0.8036626355	-4.1440134944	3.1097486158
C	0.0988193028	-5.099340968	2.3765763127
C	2.0151650775	-0.0896307773	1.5053074447
C	1.9724142011	0.4202074814	2.8151994888
C	3.2360586753	-0.0793472836	0.8159360773
C	3.1286210755	0.9006178681	3.4302971267
C	4.3891629786	0.4147030244	1.4297857328

C	4.3410044699	0.8987285121	2.7375123507
C	0.7543890425	-0.9804558683	-1.0189638278
C	0.0614837602	-0.1969055795	-1.9543146126
C	1.6546026373	-1.9555693428	-1.4865896485
C	0.2745933047	-0.3696290914	-3.3242844842
C	1.8686862393	-2.1237061256	-2.8541752673
C	1.1805236869	-1.3290899073	-3.7756556308
C	-4.6027754169	0.3268583414	2.5133306973
C	-2.5359380756	-1.4306493918	3.3632744758
C	-3.5749854898	-1.5726676515	0.6530110827
H	-2.9545385836	5.1496801312	0.3706858666
H	-2.0589174693	1.7528015676	3.8542813555
H	-1.9581461812	2.7102759649	-1.1454789488
H	-3.8335506018	2.5670059584	1.3057133932
H	1.7238760293	4.3622217027	1.7398732805
H	-0.1184137358	4.0118940567	4.2373842257
H	-0.3309946184	2.4825732467	2.9632875584
H	-0.1388716242	5.142086012	-0.6586607627
H	-2.9742213102	4.5794534924	3.3218150679
H	-0.6373952927	6.0841147489	2.2608561759
H	-0.7637035498	-3.1901728054	-0.2984999275
H	1.4986860413	-2.115829017	3.2083131194
H	-1.0099312818	-5.4810703138	0.5648318035
H	1.260296119	-4.4119078675	4.0587574183
H	-0.0014294413	-6.113804504	2.7522299392
H	1.0274134215	0.4563877355	3.3510061205
H	3.2919389116	-0.4404039419	-0.2049553355
H	3.075717517	1.2935196117	4.4416100676
H	5.325652905	0.4249991912	0.8787116568
H	5.2396174592	1.28535867	3.2100399036
H	-0.6487407774	0.5498997682	-1.6115229188
H	2.1802750493	-2.5928918016	-0.7815863538
H	-0.2698135362	0.2471749323	-4.0336526222
H	2.5694127818	-2.878585276	-3.2006130804
H	1.3471627133	-1.4636394095	-4.840941404
H	-4.4308895793	1.0748547886	3.2902942803
H	-5.13248632	0.8083984396	1.6891849491
H	-5.2164201666	-0.4870468272	2.9158721445
H	-1.6603693236	-2.039273046	3.1294930776
H	-2.2976815746	-0.7860875195	4.2149286071
H	-3.3689078495	-2.0883271771	3.6370004577
H	-2.7525067944	-2.219219649	0.3403194925
H	-4.3836126285	-2.1956143649	1.0525341731
H	-3.9443464428	-1.0268621524	-0.2206983547

Table S3. [8,8,8-(PMe₃)₃-*nido*-8,7-RhSB₉H₁₀] (**8**) (-2120.90044496)

Rh	-0.5855064654	-0.16508076	-0.0447300757
B	-0.9105861065	3.3126015263	0.316134504
B	-2.555306875	0.8989158414	0.3065103433
B	0.2249059622	1.9878086374	0.175242414
B	-1.3833035547	1.8875206063	-0.6270471303
B	-1.2017397755	1.9461405849	2.8591297766
B	-2.7807136668	1.7881543341	1.9408622921
B	-0.0596112525	2.932815936	1.8088382769
B	-2.5896716914	2.6754400415	0.4019586614
B	-1.7883625405	3.2457294124	1.8797299499
S	0.2041706067	0.947824298	1.9897967057
P	-1.4755611005	-2.1559897706	1.1483812648
P	1.7858748697	-1.0194644649	-0.3654430975
C	-1.4292074073	-3.8764581238	0.4375802708

C	-0.6315762631	-2.4543262481	2.7749600824
C	-3.2465335738	-2.1308667961	1.7008618346
C	2.1811427001	-2.8402697499	-0.3723725834
C	2.7070758767	-0.4738160663	-1.8831136263
C	2.9865379839	-0.4625571595	0.9333376067
P	-1.1852340495	-0.7069920361	-2.2558012603
C	-2.9835342091	-0.6431813252	-2.674243295
C	-0.462992874	0.2984783197	-3.6351302762
C	-0.7513111176	-2.405943266	-2.8668844038
H	-0.6498750531	4.3418716458	-0.2262121812
H	-3.5173833444	0.3307108418	-0.1089283107
H	1.3159508994	2.1228936656	-0.2830477335
H	-1.5155661923	2.0622421151	-1.7986028969
H	-1.0869391314	1.9481554699	4.0442948707
H	-3.836777159	1.7516069251	2.4951101369
H	0.837759765	3.5619108622	2.2667865821
H	-3.4909455314	3.2866891601	-0.0845113182
H	-2.2028257031	4.2081180885	2.4485205407
H	-0.4296730893	-4.1208456469	0.0694812755
H	-1.7177888282	-4.6129031734	1.1967348876
H	-2.1337855066	-3.9538852365	-0.3967668806
H	-1.084537064	-3.298912131	3.3072490831
H	0.4316231021	-2.6637096334	2.6201126534
H	-0.7118718272	-1.5578595297	3.396590408
H	-3.9074332793	-2.0402842797	0.8342049074
H	-3.4921268528	-3.0482157211	2.2484341704
H	-3.4306945689	-1.2703017285	2.3487653978
H	3.2525859947	-3.0115638061	-0.5291381183
H	1.9004048291	-3.2812240919	0.5895717677
H	1.6261339525	-3.3596960255	-1.1590406174
H	3.7678325978	-0.7413905819	-1.8154775143
H	2.2917283848	-0.9419314088	-2.7802241826
H	2.6185767074	0.6119953254	-1.9839113922
H	3.9901518375	-0.8413517733	0.7090644687
H	3.0145958059	0.629318597	0.9721075408
H	2.6782206228	-0.8239215844	1.9179254987
H	-3.1377305583	-0.9209712976	-3.7230210075
H	-3.5467175863	-1.3276417364	-2.0337555035
H	-3.3605913479	0.3669547575	-2.5022578965
H	-0.7970793915	-0.100655486	-4.5996783669
H	-0.7827324029	1.3370095991	-3.5418411248
H	0.6280076259	0.2723739923	-3.5977284822
H	-1.1398572748	-2.5512431015	-3.8812753399
H	0.3343669352	-2.5338465498	-2.8941708383
H	-1.1723584613	-3.1730451972	-2.2141452066
H	-2.4227783821	0.5999739037	1.625049488

Table S4. [8,8,8-(PPh₂Me)₂(H)-*nido*-8,7-RhSB₉H₉-9-(PPh₂Me)] (**9**) (-3271.25046267)

Rh	-1.9448817104	0.6021467084	-0.1499288951
B	-1.3513350982	-2.4145209626	-1.8412452156
B	-0.1605463937	-0.737671427	0.2003546784
B	-2.5179781426	-1.1359519127	-1.5404570437
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