

Supporting Information

Characterization of the Facile, Two-electron,
Reduction of a Closo-Rhodathiadecaborane:

Reaction of *arachno*-4-SB₈H₁₂ with



Susana Luaces, Jonathan Bould, Ramón Macías, Rodrigo Sancho, Fernando J. Lahoz
and Luis A. Oro

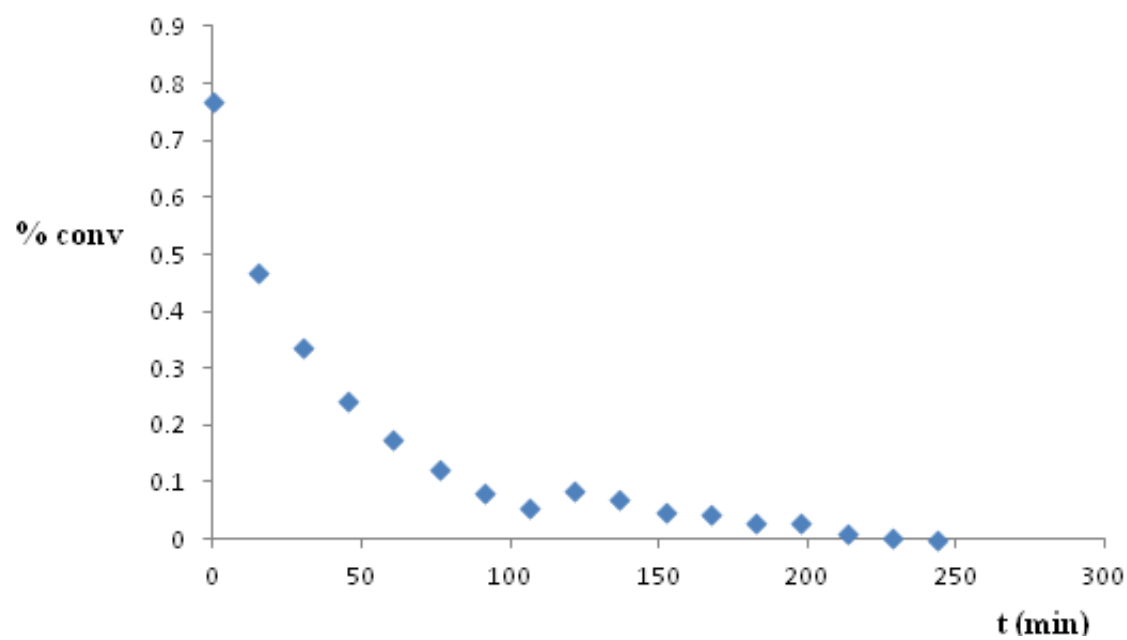


Figure S1 Plot of reaction time (minutes) vs conversion based on ^1H NMR signal intensities for reaction of **3** with PPh_3 .

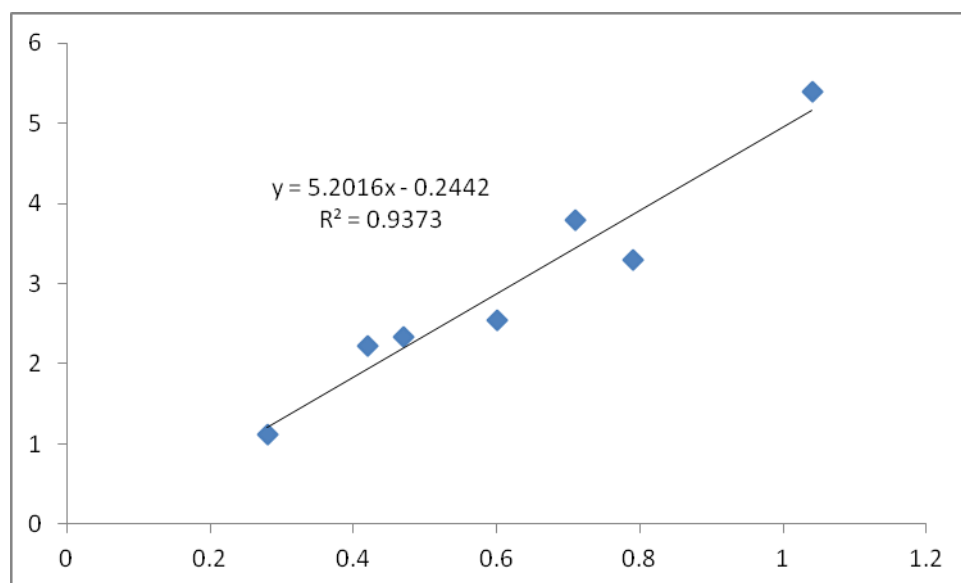


Figure S2 Plot of k_{obs} versus $[\text{PPh}_3]$

Tables of the optimized geometries (Cartesian coordinates, in Angstroms) for the calculated molecular geometry of compounds 3, 4 and 5. Energies (in Hartrees) in parenthesis.

Table S4 [2,2,2-(PPh₃)₂(H)-*closo*-2,1-RhSB₈H₈] (**3**) (-2784.64381177)

Rh	4.3761327137	4.3590663917	3.8673681246
P	6.5362667325	3.2888176191	4.3038570987
P	3.0009930516	2.3769134157	3.3981633292
S	4.5062659042	5.4913246374	1.7076331922
B	5.4389981273	6.3828108842	3.2225293378
B	4.0361310872	7.3037778376	2.244840879
B	2.8501211907	5.8437848847	2.7230496402
B	2.8914626208	5.929566886	4.5667678885
B	4.7035574583	6.3154179854	4.9254852724
B	4.5772135566	7.8230210389	3.8230943279
B	2.8081801425	7.4578541433	3.4790419322
B	3.4484328122	7.4639384339	5.0583305285
H	4.1826664527	4.0406711996	5.3901374298
H	6.6052269569	6.4460473687	3.0072682624
H	4.0758262678	8.0025860026	1.285011006
H	1.9019965769	5.4686016787	2.1211853233
H	1.9702629274	5.487053582	5.1865514897
H	5.430084643	6.230683068	5.8630436236
H	5.1690320581	8.859431206	3.8573868911
H	1.8940238446	8.1792506487	3.2153964767
H	3.1334606421	8.1234943968	5.9950103799
C	7.8052203932	3.2868410307	2.9549582516
C	7.4098842804	3.3885647996	1.6154498171
C	9.1767411632	3.1614698261	3.2432614525
C	8.3542931366	3.3695883585	0.5864776275
H	6.3591850639	3.4915422169	1.3758985747
C	10.1196796031	3.1388568219	2.2159515246
H	9.509574646	3.0886160983	4.2735518663
C	9.7109728479	3.245374244	0.8840630312
H	8.0267808086	3.4618488746	-0.4454830249
H	11.1749298092	3.0444656319	2.4577265204
H	10.4476017888	3.2373380863	0.085218124
C	7.4583847385	4.1425497421	5.6755536999
C	7.4514579224	3.6629119269	6.9925719632
C	8.1469181343	5.3366894735	5.4021085299
C	8.1082897635	4.360446196	8.0092980577
H	6.9459037187	2.7364261666	7.2384829888
C	8.8063790363	6.0280456113	6.4168675865
H	8.1690390285	5.7348088935	4.394331486
C	8.7866557532	5.545025134	7.7266829396
H	8.089979584	3.9685440235	9.0228271008

H	9.3294494751	6.9508490777	6.1815283048
H	9.2964479184	6.0872658738	8.5183772358
C	6.5171801838	1.5274457928	4.8840183298
C	7.4036034874	0.5542589756	4.3991820859
C	5.5933582602	1.1558178813	5.8748975925
C	7.376384561	-0.7470431075	4.9058702829
H	8.1188236188	0.803533159	3.6239435911
C	5.5727003947	-0.1418923764	6.3871205474
H	4.8827683044	1.8831304827	6.2501132528
C	6.4679272882	-1.0986969356	5.9048156399
H	8.0721970655	-1.4855636018	4.5163974669
H	4.8504062693	-0.4015146516	7.1563373671
H	6.4540818786	-2.1105308823	6.3011417789
C	2.1627318665	1.5570841927	4.8387847561
C	1.3526733137	0.4251875088	4.6299239908
C	2.2249689778	2.1064689818	6.125491107
C	0.6680663698	-0.1657107105	5.6902400968
H	1.2452095874	0.0110133165	3.6320337465
C	1.5287961565	1.5203572907	7.1869945275
H	2.799696599	3.0110778406	6.2934555641
C	0.7582704114	0.3781157543	6.9748160858
H	0.0526214644	-1.043145607	5.510362989
H	1.5852776779	1.9676516646	8.1756500526
H	0.2171462302	-0.0781896981	7.7993841542
C	3.8762983827	1.0221083099	2.4896567397
C	4.4522355094	1.3462079166	1.2478087724
C	4.0312767568	-0.2831092128	2.9761224607
C	5.1316669946	0.3857264524	0.4995626996
H	4.3590867607	2.356496088	0.8582648648
C	4.7244114062	-1.2412288247	2.2318307772
H	3.6274992921	-0.5574712066	3.943007578
C	5.2688013092	-0.914904022	0.9904798921
H	5.5592226714	0.6557942255	-0.4621867962
H	4.8389997434	-2.2450796846	2.6314879749
H	5.803420268	-1.6635949272	0.4122552453
C	1.4828399206	2.6575456485	2.3569584243
C	0.4565122942	3.4399722328	2.9147544215
C	1.2885754502	2.1011001523	1.0857736461
C	-0.7309506157	3.6556024191	2.2195728602
H	0.5902992989	3.8929833877	3.8922150326
C	0.0983494601	2.3261051259	0.3870678373
H	2.0507427839	1.4770293484	0.6337506689
C	-0.9137888208	3.1012596238	0.9500309012
H	-1.5101969981	4.2656211888	2.6679635142
H	-0.0335532911	1.8846134017	-0.597312085
H	-1.8387099241	3.2731645694	0.4062082124

Table S5 [6,6,9-(PPh₃)₃-*arachno*-6,5-RhSB₈H₈] (**4**) (-3820.95865915)

Rh	-5.086252932	-3.6675411317	-4.0707617099
S	-7.0796165288	-4.0817278627	-2.7307289099
P	-6.0523497209	-4.6390455283	-6.0321185263
P	-3.1001416612	-2.8393612128	-4.97094468
P	-4.930676202	-7.6603625042	-0.2112651987
B	-4.0307150104	-4.4707859964	-0.7862192568
B	-5.6491963804	-4.627416907	-0.1220417098
B	-6.8190344217	-5.2763547538	-1.225543422
B	-5.1468869698	-5.9572315145	-1.1376418145
B	-5.762389004	-2.6124924117	-2.172037341
B	-6.7634916733	-3.4837992135	-0.8419842207
B	-5.0811231077	-3.0117438367	-0.6036054963
H	-3.1264647616	-2.4249540464	-2.0824509361
H	-3.0426630019	-4.5561730884	-0.1219340462
H	-4.8631564195	-2.1707712517	0.2126487324
H	-6.1593642693	-1.5149742229	-2.417748371
H	-5.7355239412	-4.9085292159	1.031994261
H	-7.6878310888	-2.9402497112	-0.331026847
H	-7.8129341899	-5.8668757534	-0.9309213945
H	-3.7142563276	-4.3894509559	-2.0718099581
H	-4.8713912126	-6.188390992	-2.2767786239
B	-4.0879201398	-3.1258334028	-2.0660937177
C	-6.173250729	-8.889390371	-0.7817955224
C	-6.5452656114	-9.9780483062	0.0250172345
C	-6.7505524817	-8.7511398559	-2.0530041139
C	-7.4697139545	-10.915183176	-0.4376519053
H	-6.1240637146	-10.0880086279	1.019687318
C	-7.6768436111	-9.6895629977	-2.5100911714
H	-6.4961594929	-7.9014224427	-2.6770718917
C	-8.0365275045	-10.7721378245	-1.7059663452
H	-7.7525650252	-11.7505714244	0.197153218
H	-8.1259733037	-9.5566438161	-3.489647104
H	-8.7631478421	-11.4979139566	-2.061547396
C	-3.294894137	-8.4355551033	-0.5424224646
C	-3.1503465317	-9.8234514283	-0.6982516771
C	-2.1555778288	-7.6170364601	-0.6100864824
C	-1.8891433959	-10.3822530773	-0.9082258761
H	-4.020825599	-10.4698240685	-0.6632615641
C	-0.8948634575	-8.1830525197	-0.8107752503
H	-2.2528499336	-6.5413661366	-0.510550707
C	-0.758574492	-9.5643873137	-0.9603295717
H	-1.7920789949	-11.45752256	-1.0316224701
H	-0.0226716244	-7.5371350164	-0.8551018779
H	0.2232857909	-10.0020600841	-1.1202276662
C	-5.1143431	-7.6431933793	1.614403952
C	-4.0402179818	-7.9083984502	2.4736828005
C	-6.3690371777	-7.3191188818	2.1592202346

C	-4.2188147911	-7.8557480213	3.8583472315
H	-3.0649577279	-8.1557004311	2.0678096542
C	-6.5424803624	-7.2722479441	3.5407757958
H	-7.2066146908	-7.0985147885	1.504124115
C	-5.4675491901	-7.5400899013	4.393050986
H	-3.3786483009	-8.0622245601	4.5156311927
H	-7.5156611135	-7.0185931604	3.9514971008
H	-5.6042707679	-7.4990170524	5.4702678642
C	-7.5322944648	-5.7605879589	-5.808986294
C	-8.7439569437	-5.1823812941	-5.388560551
C	-7.5034917259	-7.1422862569	-6.047209943
C	-9.8865789437	-5.9609194536	-5.2102712034
H	-8.8004653637	-4.1135526744	-5.2085632413
C	-8.6527585655	-7.9209338008	-5.8753628616
H	-6.5922401093	-7.6196235874	-6.3898339537
C	-9.846698801	-7.3355389621	-5.4542387926
H	-10.8095922997	-5.4899020848	-4.8832625239
H	-8.6119492355	-8.986382098	-6.0902168031
H	-10.7395130913	-7.9413026345	-5.3235381737
C	-4.935885824	-5.7243358856	-7.0368502674
C	-4.7697643944	-5.6479745493	-8.425503023
C	-4.2131462116	-6.7007605388	-6.3274392525
C	-3.9192168902	-6.5364442259	-9.0888832764
H	-5.2863256517	-4.8849904444	-8.9962358392
C	-3.3760363386	-7.5971348924	-6.9919807484
H	-4.3147847525	-6.7575760659	-5.2460085668
C	-3.2287291903	-7.5184120395	-8.3789783851
H	-3.797088215	-6.4550699211	-10.1657311827
H	-2.8351369369	-8.351238212	-6.425937618
H	-2.5729640282	-8.2114335927	-8.8994744076
C	-6.8150018766	-3.4224117002	-7.2059509938
C	-7.5268224965	-3.8163753956	-8.352280143
C	-6.7654934229	-2.0595677567	-6.8789380848
C	-8.1337409629	-2.8657658863	-9.1728726555
H	-7.6224014622	-4.8705990028	-8.5955404457
C	-7.3832281379	-1.1077372558	-7.6952206247
H	-6.2517048177	-1.756946444	-5.9693327172
C	-8.0597622026	-1.5082300658	-8.8477360224
H	-8.6758425348	-3.1853585762	-10.0591599514
H	-7.3393566217	-0.0561610509	-7.4241228489
H	-8.5408689828	-0.7693191597	-9.4833221581
C	-2.682195345	-3.0066293992	-6.7863171799
C	-3.394253308	-2.2206693713	-7.7089803869
C	-1.67308825	-3.848627813	-7.2743697539
C	-3.1051610329	-2.2710768389	-9.0718543756
H	-4.1699203868	-1.5474407722	-7.36093252
C	-1.3823860825	-3.8993300853	-8.6406674532
H	-1.0975489706	-4.4630344789	-6.5917537433

C	-2.0935492775	-3.1108512472	-9.5441336771
H	-3.6670656919	-1.6472722374	-9.762308016
H	-0.5914777612	-4.5563403749	-8.9934467745
H	-1.8610328213	-3.1462383968	-10.6054282382
C	-2.8289832381	-1.0055093744	-4.8096427709
C	-1.7664894286	-0.3650247361	-5.4737723614
C	-3.7074618742	-0.2278574758	-4.0441283375
C	-1.5811345979	1.0123102523	-5.3584855393
H	-1.0851591623	-0.9431023325	-6.0907346945
C	-3.5248741989	1.1535707968	-3.9348225149
H	-4.53493822	-0.7054274332	-3.5340160039
C	-2.4616491324	1.7763310713	-4.5876872588
H	-0.7528620785	1.4892268324	-5.8764043946
H	-4.2175999137	1.7384569137	-3.3355060444
H	-2.3197854949	2.8506530661	-4.50193487
C	-1.5918830483	-3.6023551603	-4.1939741667
C	-0.5147845873	-2.8642365453	-3.6850317613
C	-1.541806463	-5.0035699084	-4.1114056058
C	0.5902399122	-3.5108163019	-3.125959159
H	-0.5362249354	-1.7807302754	-3.711514323
C	-0.4299421013	-5.6504915602	-3.5707827538
H	-2.3799668355	-5.5893004633	-4.4760748897
C	0.6417252947	-4.9039749744	-3.0751500077
H	1.4115421781	-2.919703247	-2.7289967628
H	-0.4090063393	-6.7360092561	-3.5262218843
H	1.5078029918	-5.4038807244	-2.6484499363

Table S6 [2,2,2-(Cl)(H)(PPh₃)-6-(PPh₃)-*closo*-2,1-RhSB₈H₇] (**5**) (-3058.85832561)

Rh	4.4880089424	6.3808185257	4.0831350833
H	6.0078405233	6.7242107601	3.9655126007
Cl	4.718513457	4.6281801715	2.346024501
S	2.2354645599	5.7370301749	4.742044783
P	4.4091651507	7.9701786673	2.351658605
P	6.9096609801	4.7688308633	6.3420542473
C	4.8217240879	9.6875827287	2.8987832725
C	6.0815587029	10.2404971652	2.623426213
H	6.8019072987	9.6842694227	2.0335421459
C	6.4194509692	11.5093783723	3.0986325638
H	7.3989606902	11.9225194722	2.8721540882
C	5.5047707491	12.2463036002	3.8510561502
H	5.7677817878	13.2349268762	4.217628086
C	4.2483984455	11.7048129206	4.1309887669
H	3.5288032957	12.2674361542	4.719426859
C	3.9111465664	10.4347669644	3.6645093612
H	2.9358906517	10.0253050649	3.9009176595
C	2.7554314027	8.096572605	1.5411665278
C	2.1967205476	9.3159775423	1.1261179618

H	2.7239175749	10.2473958313	1.3029338329
C	0.956071041	9.3414352563	0.4847972701
H	0.5323502509	10.2927858693	0.174013851
C	0.2646877972	8.1532142705	0.2455635759
H	-0.7019160964	8.1756636643	-0.2507283031
C	0.8204234871	6.9355804176	0.6447638419
H	0.2911248159	6.0054954083	0.4565690663
C	2.056760941	6.9032877049	1.2899255222
H	2.4930631815	5.953823359	1.5865112231
C	5.5749970505	7.7039124368	0.9443231379
C	5.2912360242	8.2438513209	-0.3199040453
H	4.3568026283	8.7682602264	-0.4920444142
C	6.2015666597	8.1061566023	-1.3683091772
H	5.965241715	8.5241365088	-2.3432475906
C	7.4070160277	7.4317916306	-1.1659364367
H	8.1145879092	7.3224650831	-1.9837355933
C	7.6949967245	6.8912051177	0.0882011968
H	8.6249156245	6.3538436825	0.2529121803
C	6.783005602	7.0186799963	1.1367816928
H	6.9985991203	6.5684018547	2.0982170798
C	6.8860777821	2.9892403301	5.9001235653
C	6.1937767943	2.5662297727	4.7542386832
H	5.6579763319	3.2733471192	4.1284517235
C	6.2038020619	1.2173949339	4.3953042187
H	5.6641935777	0.9048419086	3.5059813223
C	6.8934301995	0.2836486973	5.1702417038
H	6.8926813153	-0.766193605	4.8890758681
C	7.5858396011	0.7013468855	6.3087180208
H	8.1263739914	-0.0190264478	6.9166068174
C	7.5859912105	2.04742997	6.6744264991
H	8.1276589795	2.3580267301	7.5608075056
C	8.1936444261	5.5660031127	5.3050751239
C	8.3595172177	6.9601706081	5.3809281986
H	7.7145281877	7.5541861801	6.0208660042
C	9.3446772605	7.5882402619	4.6205662598
H	9.4643488924	8.6660105321	4.6842226649
C	10.1645123257	6.8368586329	3.7734253974
H	10.9288146273	7.3299233882	3.1788128324
C	9.998346762	5.4539522218	3.6907798063
H	10.6306556721	4.8649653077	3.0322583124
C	9.0174653671	4.8167757573	4.4552563277
H	8.892197653	3.7418733104	4.3820628159
C	7.5808690005	4.806904868	8.0541207761
C	8.8865526257	5.2377315562	8.3279790476
H	9.5265019978	5.5869899228	7.5253059355
C	9.3725838247	5.2228937729	9.6375699325
H	10.3848142578	5.5635383978	9.8371711318
C	8.564126155	4.7735566016	10.6813379145

H	8.9434037192	4.7639750272	11.6995390797
C	7.2638240739	4.3374376988	10.4143806285
H	6.6266974704	3.989919346	11.2226348555
C	6.7720273067	4.3545310425	9.110578753
H	5.7563943287	4.0259758667	8.9192257726
B	5.1848271405	5.7207555168	6.194891612
B	4.7444534522	7.5545830632	5.9143922318
H	5.3581588258	8.5665667451	5.7729480138
B	2.9366533225	7.4367761493	5.4619968452
H	2.2737925148	8.3582343758	5.1135662392
B	3.6546108925	4.8440315645	5.8067033452
H	3.5795998027	3.6650974569	5.6944844663
B	4.9859800202	6.8346320977	7.4550365753
H	5.7328206851	7.1769452378	8.3115559929
B	3.3800599738	7.3304403372	7.1929982316
H	2.8948485052	8.1158078547	7.9481337999
B	2.3480435614	6.0057760204	6.647073607
H	1.3009515935	5.7813667633	7.1612718648
B	3.8391572899	5.568078863	7.4486742515
H	3.7202685353	4.8614009525	8.4025360383