Electronic Supplementary Information

DFT calculations of ^{29}Si-NMR chemical shifts in Ru(II) silyl complexes. Searching for trends and accurate values.

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Optimized geometries

Optimized geometries of all structures reported in the article. The optimizations use a triple-ζ basis set on the Si atom (cc-pvtz). Each structure is accompanied by the following energies in a. u.: 1) zero-point energy (E) 2) enthalpy (H) and 3) Gibb's free energy (G)

$RuCp(PMe_3)_2SiH_3$

E = -832.038398 a.u.

H = -832.014513 a.u.

G = -832.088927 a.u.

Ru	0.488157	-0.174392	0.267709
C	1.350048	-0.454143	-1.795975
C	2.334214	0.156751	-0.964919
C	1.081933	-1.764822	-1.266896
C	2.660480	-0.752433	0.084083
C	1.883304	-1.945887	-0.113788
H	0.935024	-0.031245	-2.700668
H	2.773393	1.133757	-1.117962
H	0.412019	-2.498839	-1.694318
H	3.401350	-0.590398	0.854692
H	1.925677	-2.841440	0.492804
P	0.164482	-0.542370	2.499778
C	1.737252	-0.939794	3.410433
C	-0.520507	0.742837	3.656726
C	-0.871107	-2.016332	2.992262
P	-1.725962	0.003594	-0.257561
Si	0.537907	2.151468	0.674976
H	1.545507	-1.130968	4.471029
H	2.208543	-1.820201	2.967391

H	2.418370	-0.091298	3.310891
H	-0.565583	0.353674	4.678897
H	0.126720	1.623217	3.632308
H	-1.519329	1.049451	3.342425
H	-0.848395	-2.189743	4.073436
H	-1.907124	-1.858665	2.680164
H	-0.491813	-2.899928	2.472191
C	-2.986776	0.687875	0.925548
C	-2.106410	1.049175	-1.748526
C	-2.580984	-1.581113	-0.746195
H	-3.632170	-1.412402	-1.002802
H	-2.067040	-2.012633	-1.608706
H	-2.515668	-2.292888	0.080475
H	-3.968687	0.746436	0.445972
H	-3.064833	0.047079	1.807263
H	-2.674790	1.686775	1.237995
H	-3.175186	1.045200	-1.986843
H	-1.776578	2.072643	-1.552975
H	-1.542960	0.668469	-2.603760
H	-0.672433	2.839834	1.262255
H	1.629530	2.620706	1.609439
H	0.789901	2.989133	-0.555467

$RuCp(PMe_3)_2SiMeH_2$

E = -871.320907 a.u.

H = -871.295404 a.u.

G = -871.373078 a.u.

Ru	0.291278	-0.191322	0.231290
C	0.829380	-0.913331	-1.841094
C	1.745009	0.107080	-1.459526
C	0.995772	-2.034393	-0.962071
C	2.470189	-0.358363	-0.314282
C	1.992838	-1.674117	-0.015013
H	0.165411	-0.871517	-2.694952
H	1.886584	1.051681	-1.964559
H	0.479648	-2.982714	-1.022203
H	3.271141	0.163126	0.191569
H	2.362102	-2.312222	0.777803
P	0.101977	-0.558223	2.478725
C	1.734077	-0.467219	3.367625
C	-0.912221	0.495765	3.628283
C	-0.473934	-2.254002	3.005841
P	-1.935826	-0.043737	-0.239872
Si	0.293624	2.119819	0.763636
H	1.623652	-0.710130	4.429321
H	2.443500	-1.161598	2.912026
H	2.124474	0.548221	3.263618
H	-0.703123	0.222235	4.667069
H	-0.660224	1.547489	3.473068
H	-1.976340	0.358539	3.433727
H	-0.428280	-2.381328	4.092910
H	-1.502782	-2.405735	2.668141
H	0.154681	-3.008545	2.525700
C	-3.237578	0.398226	1.010952
C	-2.395946	1.149355	-1.594457
C	-2.687529	-1.610952	-0.917501
H	-3.743194	-1.474629	-1.175413
H	-2.138640	-1.922333	-1.809744
H	-2.593179	-2.399721	-0.166685
H	-4.215189	0.491524	0.527883
H	-3.294891	-0.384451	1.771695
H	-2.975765	1.346262	1.485419
H	-3.457025	1.076728	-1.855273
H	-2.173206	2.165063	-1.257881
H	-1.789805	0.939282	-2.479306
H	-1.051798	2.742364	1.090437
H	1.065524	2.486186	2.017441
C	1.011206	3.332971	-0.526542
H	0.914036	4.366437	-0.176431
H	2.075702	3.142194	-0.701960
H	0.494554	3.252529	-1.489570

$RuCp(PMe_3)_2SiMe_2H$

E = -1580.041439 a.u.

H = -1580.014442 a.u.

G = -1580.094104 a.u.

Ru	0.025280	-0.022146	-0.000685
C	0.061391	-0.019114	2.239971
C	1.401944	0.034565	1.758976
C	-0.603176	1.183057	1.814799
C	1.565559	1.243431	1.024231
C	0.317578	1.956316	1.067999
H	-0.354767	-0.793325	2.869664
H	2.173840	-0.698674	1.948540
H	-1.621517	1.463884	2.048861
H	2.483251	1.584215	0.565379
H	0.123252	2.929114	0.634824
P	0.219550	0.803501	-2.108665
C	1.643983	1.967008	-2.325274
C	0.468809	-0.241449	-3.614195
C	-1.151663	1.893765	-2.724234
P	-1.969646	-1.034866	-0.376697
Si	1.184722	-1.999620	-0.657813
H	1.667526	2.379202	-3.339783
H	1.563991	2.790425	-1.611286
H	2.579182	1.435067	-2.132872
H	0.535166	0.385171	-4.510037
H	1.389140	-0.820743	-3.512512
H	-0.352912	-0.949640	-3.732283
H	-0.896488	2.366649	-3.679317
H	-2.062473	1.303811	-2.859704
H	-1.359231	2.669477	-1.982094
C	-2.387880	-1.850611	-1.981013

C	-2.447599	-2.393337	0.785802
C	-3.468716	0.045915	-0.184773
H	-4.393494	-0.506117	-0.387346
H	-3.507702	0.433976	0.836606
H	-3.403221	0.898309	-0.865358
H	-3.358169	-2.354112	-1.918585
H	-2.435124	-1.106899	-2.780965
H	-1.613721	-2.580778	-2.228958
H	-3.485418	-2.706568	0.627681
H	-1.788500	-3.251278	0.635186
H	-2.330139	-2.050451	1.816979
H	0.639368	-2.747842	-1.857279
C	3.019869	-1.712560	-1.136367
C	1.311327	-3.390884	0.655522
H	1.860568	-4.247855	0.246780
H	1.847806	-3.055286	1.550749
H	0.331914	-3.752445	0.984631
H	3.504756	-2.652123	-1.428054
H	3.130735	-1.007694	-1.967808
H	3.581032	-1.300110	-0.288944

$RuCp(PMe_3)_2SiMe_3$

E = -949.880968 a.u.

H = -949.852044 a.u.

G = -949.935658 a.u.

Ru	0.372710	-0.138113	0.209975
C	0.971754	-0.481707	-1.948342
C	1.994302	0.265462	-1.304725
C	0.897663	-1.776850	-1.328747
C	2.540636	-0.539850	-0.256631
C	1.857254	-1.800481	-0.286765
H	0.397264	-0.149073	-2.801546
H	2.321423	1.257253	-1.583981
H	0.253033	-2.594095	-1.623611
H	3.363212	-0.271612	0.391025
H	2.067213	-2.643708	0.357775
P	0.138300	-0.768956	2.391064
C	1.594775	-0.445693	3.505089
C	-1.248433	-0.209344	3.499595
C	-0.036539	-2.611412	2.664988
P	-1.869048	0.085433	-0.178735
Si	0.624252	2.175873	0.802739
H	1.469242	-0.925317	4.481535
H	2.495757	-0.833219	3.022906
H	1.716834	0.630922	3.641643
H	-1.110194	-0.605626	4.510515
H	-1.279340	0.879676	3.539121
H	-2.200114	-0.578075	3.108575
H	-0.129737	-2.849022	3.730176
H	-0.919767	-2.976831	2.134955
H	0.837992	-3.127132	2.262362
C	-2.984426	1.312675	0.669200
C	-2.311599	0.484469	-1.945479
C	-2.907590	-1.455278	0.024816
H	-3.937887	-1.298271	-0.312555
H	-2.453088	-2.261374	-0.557072
H	-2.918930	-1.758299	1.074879
H	-4.011104	1.208716	0.303511
H	-2.970922	1.158103	1.749016
H	-2.629160	2.324199	0.462811
H	-3.396117	0.568714	-2.069676
H	-1.838309	1.425919	-2.233206
H	-1.941131	-0.307921	-2.600267
C	-0.215538	2.973862	2.334613
C	2.451658	2.658400	1.138041
C	0.125344	3.375330	-0.611198
H	0.354479	4.414241	-0.340759
H	0.666671	3.148800	-1.537226
H	-0.944559	3.328091	-0.845886
H	2.524861	3.735532	1.336410
H	2.854940	2.137789	2.014092
H	3.115834	2.437199	0.296009
H	-0.001637	4.050525	2.327694
H	-1.303418	2.860338	2.361753
H	0.185516	2.580687	3.276252

$RuCp(PMe_3)_2SiH_2Cl$

E = -846.535180 a.u.

H = -846.510189 a.u.

G = -846.587304 a.u.

Ru	0.462059	-0.191634	0.288029
C	1.058517	-0.845241	-1.792085
C	2.096046	-0.039928	-1.248241
C	0.947890	-2.037555	-0.996040
C	2.621142	-0.708360	-0.095113
C	1.901444	-1.939012	0.048799
H	0.495775	-0.624684	-2.689726
H	2.440692	0.904456	-1.647782
H	0.276743	-2.866667	-1.170744
H	3.449777	-0.374084	0.513431
H	2.077958	-2.688570	0.809982
P	0.173727	-0.552979	2.533623
C	1.790562	-0.709620	3.439015
C	-0.693038	0.621234	3.680487
C	-0.644473	-2.156308	3.019034
P	-1.748087	0.115382	-0.260807
Si	0.801572	2.069914	0.755828
H	1.632691	-0.927867	4.499969
H	2.390558	-1.506584	2.994150
H	2.334267	0.232961	3.338646
H	-0.633892	0.247650	4.707588
H	-0.221095	1.604310	3.622641

H	-1.740273	0.730855	3.397664
H	-0.608943	-2.315132	4.101935
H	-1.687947	-2.144759	2.693659
H	-0.139960	-2.983441	2.513154
C	-3.072653	0.533753	0.970064
C	-2.089678	1.392005	-1.567090
C	-2.527486	-1.379658	-1.056363
H	-3.567305	-1.180896	-1.336025
H	-1.964911	-1.651918	-1.952817
H	-2.493542	-2.220162	-0.358723
H	-4.037487	0.635502	0.463377
H	-3.148339	-0.260631	1.717193
H	-2.820532	1.476204	1.459721
H	-3.136175	1.365618	-1.888059
H	-1.856027	2.379337	-1.162835
H	-1.440135	1.204632	-2.425560
Cl	-0.828384	3.406012	1.294539
H	1.716796	2.392876	1.909156
H	1.387833	2.884966	-0.361255

$RuCp(PMe_3)_2SiHMeCl$

E = -885.821280 a.u.

H = -885.794479 a.u.

G = -885.874890 a.u.

Ru	0.305211	-0.334039	0.326396
C	1.173315	-1.027485	-1.638896
C	2.241152	-0.681322	-0.751946
C	0.481088	-2.141931	-1.059030
C	2.193395	-1.561559	0.366423
C	1.108482	-2.484242	0.163570
H	0.965757	-0.571531	-2.596767
H	2.979213	0.093677	-0.913972
H	-0.363230	-2.658731	-1.497395
H	2.896724	-1.573412	1.188409
H	0.831137	-3.300977	0.815735
P	0.131839	-0.154899	2.607119
C	1.548462	0.680802	3.472647
C	-1.294830	0.649046	3.481193
C	0.147879	-1.803422	3.479350
P	-1.915791	-0.005673	-0.157085
Si	0.836215	1.934668	0.162259
H	1.458270	0.590633	4.559976
H	2.487485	0.227492	3.145372
H	1.561314	1.737035	3.194026
H	-1.147423	0.595916	4.564402
H	-1.352566	1.695349	3.175251
H	-2.228092	0.140496	3.226943
H	0.109561	-1.679068	4.566524
H	-0.710327	-2.394748	3.150406
H	1.060240	-2.343671	3.214638
C	-3.067345	-1.351459	0.429992
C	-2.897961	1.497266	0.312553
C	-2.290588	-0.046642	-1.981449
H	-3.367993	0.022225	-2.163305
H	-1.789132	0.792827	-2.468375
H	-1.912399	-0.974174	-2.417467
H	-4.084143	-1.211227	0.048184
H	-2.681521	-2.317312	0.093722
H	-3.095247	-1.359456	1.522607
H	-3.930937	1.393305	-0.034676
H	-2.889454	1.633763	1.394044
H	-2.445597	2.384088	-0.135467
Cl	-0.147617	3.428740	1.414288
H	2.249845	2.231224	0.594505
C	0.712332	2.792486	-1.528163
H	1.122923	3.805837	-1.472473
H	1.279904	2.231539	-2.280273
H	-0.323463	2.866889	-1.875310

$RuCp(PMe_3)_2SiMe_2Cl$

E = -1594.541080 a.u.

H = -1594.512990 a.u.

G = -1594.594922 a.u.

Ru	0.046125	0.039733	-0.047881
C	0.120193	0.063970	2.192013
C	1.447204	0.171709	1.691266
C	-0.607673	1.233075	1.779863
C	1.546955	1.382778	0.939523
C	0.268533	2.029096	1.003669
H	-0.249405	-0.726499	2.831982
H	2.249830	-0.527100	1.879467
H	-1.630559	1.474781	2.033548
H	2.440143	1.771806	0.470612
H	0.021092	2.986659	0.562958
P	-0.266006	1.059930	-2.066939
C	1.007035	2.351331	-2.440678
C	-0.314305	0.213059	-3.704542
C	-1.801985	2.090750	-2.191154
P	-1.731289	-1.393564	-0.172029
Si	1.506647	-1.575796	-0.963969
H	0.763729	2.886430	-3.364887
H	1.067753	3.071275	-1.621241
H	1.984995	1.877244	-2.550632
H	-0.446216	0.950766	-4.503335
H	0.613027	-0.339273	-3.868078
H	-1.132863	-0.506445	-3.743059
H	-1.830655	2.669636	-3.120962
H	-2.684562	1.447174	-2.149158
H	-1.845571	2.774820	-1.339743
C	-2.596290	-1.807843	-1.748993
C	-1.501291	-3.092860	0.515239
C	-3.188214	-0.848757	0.837140

H	-4.007205	-1.572682	0.766380
H	-2.899842	-0.748903	1.886922
H	-3.538859	0.124655	0.484417
H	-3.422694	-2.501021	-1.558956
H	-3.000832	-0.901784	-2.207511
H	-1.886656	-2.275102	-2.435207
H	-2.454595	-3.629581	0.568515
H	-0.812572	-3.648133	-0.125794
H	-1.068667	-3.027535	1.517243
Cl	0.733862	-2.950587	-2.503789
C	3.055351	-0.941202	-1.873903
C	2.215697	-2.876939	0.238787
H	2.707051	-3.679362	-0.322052
H	2.967910	-2.425432	0.897108
H	1.443240	-3.325675	0.869676
H	3.701690	-1.775261	-2.169613
H	2.798935	-0.382513	-2.778937
H	3.631001	-0.274157	-1.220148

$RuCp(PMe_3)_2SiHCl_2$

E = -861.032350 a.u.

H = -861.006134 a.u.

G = -861.086421 a.u.

Ru	0.454188	-0.079247	0.250756
C	1.164514	-0.145323	-1.884032
C	2.220136	0.346099	-1.062419
C	0.897756	-1.503227	-1.492716
C	2.586771	-0.681874	-0.143991
C	1.770271	-1.830646	-0.426831
H	0.694016	0.396169	-2.692259
H	2.674520	1.325397	-1.131271
H	0.177459	-2.169482	-1.949550
H	3.378506	-0.617872	0.589108
H	1.829118	-2.789774	0.070122
P	0.249831	-0.745831	2.441381
C	1.807799	-0.628594	3.445857
C	-0.962617	0.046519	3.604457
C	-0.167613	-2.541249	2.728373
P	-1.805367	0.136887	-0.123461
Si	0.535641	2.121029	0.914943
H	1.651752	-1.011224	4.459634
H	2.591189	-1.213966	2.957722
H	2.135669	0.412453	3.486511
H	-0.835480	-0.349755	4.616402
H	-0.810229	1.128317	3.616070
H	-1.983336	-0.159850	3.272564
H	-0.175355	-2.775222	3.798118
H	-1.146159	-2.772823	2.301755
H	0.578241	-3.166067	2.231372
C	-2.834522	1.457539	0.680966
C	-2.229037	0.469258	-1.901637
C	-2.872115	-1.358882	0.192752
H	-3.883168	-1.217303	-0.203038
H	-2.411686	-2.228725	-0.282366
H	-2.938184	-1.547364	1.267378
H	-3.884404	1.349326	0.391419
H	-2.750369	1.403701	1.767612
H	-2.469712	2.435683	0.357520
H	-3.313337	0.531777	-2.037433
H	-1.770621	1.415325	-2.199168
H	-1.834896	-0.330048	-2.533912
Cl	0.217439	3.540901	-0.667473
H	-0.361966	2.724648	1.949965
Cl	2.421652	2.776550	1.698006

$RuCp(PMe_3)_2SiMeCl_2$

E = -900.320640 a.u.

H = -900.292860 a.u.

G = -900.375132 a.u.

Ru	0.325465	-0.091050	0.260706
C	0.829797	-0.856900	-1.804705
C	1.775137	0.143677	-1.449424
C	0.977378	-1.964246	-0.904610
C	2.501666	-0.319017	-0.302665
C	1.998468	-1.616074	0.021071
H	0.158488	-0.811393	-2.652234
H	1.937713	1.072236	-1.977077
H	0.437916	-2.900397	-0.940395
H	3.312553	0.197014	0.192531
H	2.361319	-2.249535	0.819644
P	0.112716	-0.542471	2.512974
C	1.737546	-0.667536	3.406686
C	-0.805709	0.529286	3.714622
C	-0.609001	-2.214360	2.906262
P	-1.927173	-0.039059	-0.199338
Si	0.432396	2.196034	0.660253
H	1.575993	-0.909823	4.461911
H	2.358605	-1.443583	2.954568
H	2.252700	0.291705	3.324769
H	-0.760420	0.082958	4.713029
H	-0.342497	1.517550	3.734952
H	-1.847302	0.645496	3.416097
H	-0.508689	-2.450808	3.970619
H	-1.667685	-2.236680	2.635723
H	-0.088256	-2.970812	2.313708
C	-3.245253	0.268579	1.070074
C	-2.470698	1.143127	-1.526678
C	-2.562949	-1.644499	-0.905144
H	-3.620372	-1.561214	-1.176468
H	-1.987531	-1.915402	-1.793540
H	-2.443272	-2.437942	-0.162587
H	-4.232824	0.235560	0.599366

H	-3.198968	-0.499328	1.846122
H	-3.087246	1.250869	1.518293
H	-3.523172	0.990561	-1.786743
H	-2.331318	2.164652	-1.165463
H	-1.852659	0.998377	-2.416580
Cl	-1.295781	3.255775	1.431579
Cl	1.906957	2.793898	2.133293
C	0.903199	3.385630	-0.734825
H	0.855794	4.417772	-0.376800
H	1.924105	3.190287	-1.079007
H	0.220748	3.276537	-1.584784

$RuCp(PMe_3)_2SiCl_3$

E = -875.528700 a.u.

H = -875.501348 a.u.

G = -875.583852 a.u.

Ru	0.476849	-0.107630	0.274405
C	1.145747	-0.709151	-1.790028
C	2.198489	0.016882	-1.164870
C	0.942888	-1.922746	-1.043815
C	2.631781	-0.715922	-0.017459
C	1.850724	-1.916694	0.043182
H	0.642721	-0.425989	-2.704616
H	2.605175	0.958097	-1.508335
H	0.242021	-2.711250	-1.279023
H	3.435185	-0.433982	0.648060
H	1.951862	-2.703397	0.779723
P	0.191893	-0.512927	2.531062
C	1.795582	-0.796719	3.423412
C	-0.612759	0.653409	3.726389
C	-0.709519	-2.093543	2.933043
P	-1.764004	0.082691	-0.251701
Si	0.684016	2.159074	0.609951
H	1.614631	-1.038060	4.475478
H	2.346352	-1.617140	2.958252
H	2.395497	0.113532	3.355380
H	-0.615682	0.206382	4.725472
H	-0.053903	1.590956	3.747379
H	-1.637053	0.874024	3.425177
H	-0.705590	-2.294992	4.009207
H	-1.743821	-2.025882	2.586660
H	-0.228084	-2.921742	2.406942
C	-3.071194	0.484229	1.003243
C	-2.201253	1.296102	-1.586071
C	-2.488952	-1.473310	-0.973792
H	-3.549556	-1.336723	-1.207743
H	-1.955557	-1.735145	-1.890790
H	-2.376301	-2.292806	-0.259707
H	-4.052623	0.521492	0.520387
H	-3.091952	-0.279777	1.784142
H	-2.851550	1.454838	1.451151
H	-3.257751	1.210763	-1.859990
H	-1.993812	2.309486	-1.236302
H	-1.579282	1.106572	-2.464086
Cl	-0.861043	3.356784	1.482450
Cl	2.341132	2.755369	1.818100
Cl	1.046780	3.325194	-1.139815

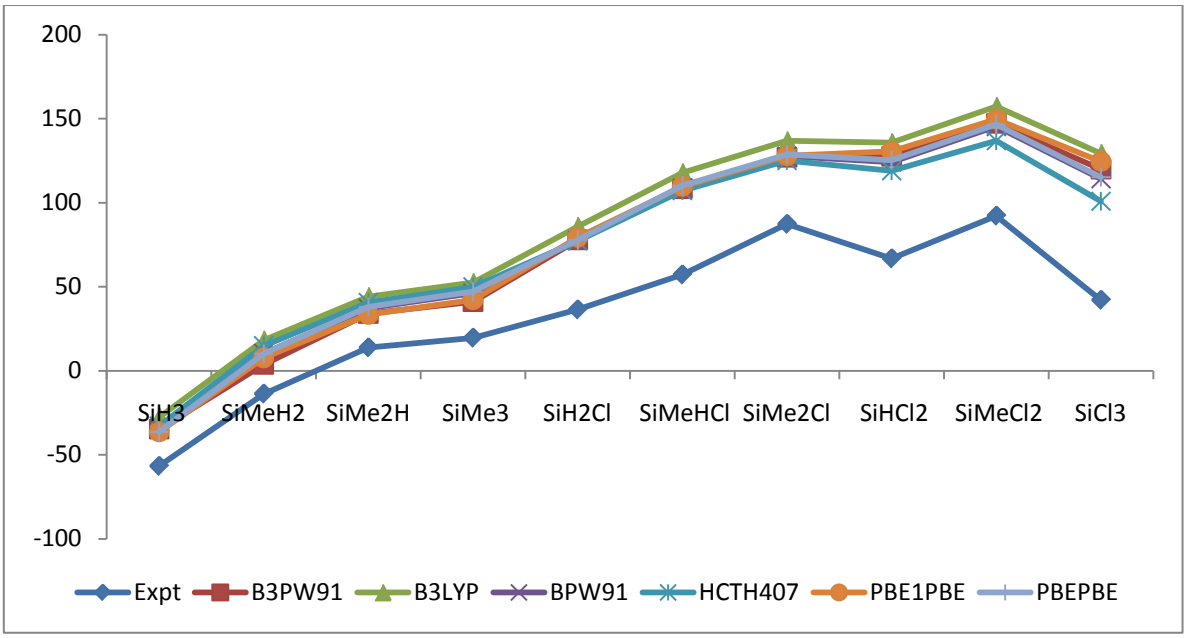
Tables and Graphs

- The solvent effect has been computed using Gaussian PCM-UFF method with dichloromethane as a solvent (ε = 8.93)
- **Table S1: ^{29}Si δ-NMR computed with different DFT functionals**

The dzvp basis set has been used in all case for the Si atom. See references below.

	SiH_3	$SiMeH_2$	$SiMe_2H$	$SiMe_3$	SiH_2Cl	SiMeHCl	$SiMe_2Cl$	$SiHCl_2$	$SiMeCl_2$	$SiCl_3$
Expt	**-56.68**	**-13.75**	**13.85**	**19.56**	**36.37**	**57.17**	**87.29**	**66.79**	**92.16**	**42.11**
B3PW91	-34.72	3.65	34.06	41.05	77.85	108.36	126.88	127.47	147.14	119.88
B3LYP	-27.65	18.24	44.11	52.44	85.87	117.81	136.80	135.70	157.22	129.24
BPW91	-34.28	10.38	37.23	46.12	77.61	108.64	127.64	124.16	145.36	114.18
HCTH407	-32.85	14.85	40.67	49.89	77.23	107.24	125.06	119.01	136.90	100.91
PBE1PBE	-36.49	7.64	33.48	42.24	79.40	109.71	127.90	130.51	149.60	124.53
PBEPBE	-36.35	10.21	38.04	47.08	77.74	110.28	128.74	125.20	146.62	115.16

Table S1 – ^{29}Si δ-NMR computed with different DFT functionals (values in ppm)



Graph S1 – Representation of ^{29}Si δ-NMR vs SiX_3 silyl substituents

- **Table S2: ^{29}Siδ-NMR computed with different DFT functionals and Si basis sets**

The modifications has been done only with SiX_3 = SiH_3 and $SiMe_3$ system. See text.

SiX_3	functional	Si Basis set	σ Si (ppm)	δ Si (ppm)
SiH_3	HCTH407	dzvp	334.83	-32.85
		cc-pvtz	395.85	-38.49
		igloIII	373.04	-31.67
	PBEPBE	dzvp	347.44	-36.35
		cc-pvtz	385.28	-43.70
		igloIII	369.99	-42.15
$SiMe_3$	HCTH407	dzvp	252.09	49.89
		cc-pvtz	310.45	46.89
		igloIII	291.17	50.20
	PBEPBE	dzvp	264.02	47.08
		cc-pvtz	298.67	42.91
		igloIII	285.28	42.55

Table S2 - ^{29}Siδ-NMR computed with different DFT functionals and Si basis sets

- ## Table S3: Scalar relativistic effects

The following DKH, ZORA, IORA and IORA mm approximations has been computed with the ORCA program and using an all-electron basis set for Si (def2-TZV)

SiX_3	Scalar approximation	σ Si (ppm)	δ Si (ppm)
SiH_3	DKH	380.20	-5.60
	ZORA	412.50	-37.10
	IORA	412.40	-37.40
	IORA mm	412.40	-37.40
$SiMe_3$	DKH	---	---
	ZORA	334.20	41.20
	IORA	334.50	40.50
	IORA mm	334.50	40.50

Table S3 - ^{29}Si δ and σ computed with the inclusion of scalar relativistic effects using DKH. ZORA. IORA and IORAmm approximations

- ## Table S4: Spin-orbit and scalar relativistic effects using the ZORA approximation

Calculation done by the ADF program

SiX_3	σ SO	δ SO
SiH_3	407.37	-57.92
$SiMeH_2$	361.08	-11.63
$SiMe_2H$	329.31	20.14
$SiMe_3$	326.64	22.81
SiH_2Cl	307.89	41.56
SiHMeCl	270.22	79.23
$SiMe_2Cl$	251.18	98.27
$SiHCl_2$	271.71	77.74
$SiMeCl_2$	248.78	100.67
$SiCl_3$	296.63	52.82

Table S4 - ^{29}Si δ and σ computed with the inclusion of scalar and SO relativistic effects using the ZORA approximation with the ADF program

- ## Table S5: ^{29}Si-σ for all systems

In all case the shielding has been computed using an all-electron basis set for Si (dzvp). The ^{29}Si-σ reported includes the inclusion of scalar relativistic effects (σ_{scalar}) and the inclusion of SO effects (σ_{so}). The last two columns is the ^{29}Si-σ computed using solvent (PCM) correction.

SiX_3	σ scalar	σ SO	σ scalar.PCM	σ SO.PCM
SiH_3	352.92	371.11	346.27	367.65
$SiMeH_2$	314.55	334.12	302.07	323.24
$SiMe_2H$	284.14	301.27	272.77	290.35

$SiMe_3$	277.15	297.14	267.32	288.56
SiH_2Cl	240.35	262.00	229.60	254.63
SiHMeCl	209.84	231.52	194.28	219.11
$SiMe_2Cl$	191.32	215.62	174.86	200.93
$SiHCl_2$	190.72	221.03	181.65	208.75
$SiMeCl_2$	171.06	204.54	157.43	192.32
$SiCl_3$	198.32	233.72	198.54	234.36

Table S5 - ^{29}Si σ computed with the inclusion of scalar relativistic effects and SO correction by perturbation theory. PCM(DCM) ^{29}Si σ is also included (values in ppm)

- ## Table S6: ^{29}Si-δ for all systems

In all case the shielding has been computed using an all-electron basis set for Si (dzvp). The ^{29}Si-δ reported includes the inclusion of scalar relativistic effects (δ_{scalar}) and the inclusion of SO effects (δ_{so}). The last two columns is the ^{29}Si-σ computed using solvent (PCM) correction.

SiX_3	δ scalar	δ SO	δ scalar. PCM	δ SO. PCM
SiH_3	-34.72	-52.91	-27.79	-49.10
$SiMeH_2$	3.65	-15.92	169.8	-4.75
$SiMe_2H$	34.06	16.93	45.43	27.84
$SiMe_3$	41.05	21.06	51.17	29.93
SiH_2Cl	77.85	56.20	88.88	63.85
SiHMeCl	108.36	86.68	124.21	99.38
$SiMe_2Cl$	126.88	102.57	143.33	117.26
$SiHCl_2$	127.47	97.17	136.83	109.73
$SiMeCl_2$	147.14	113.66	161.05	126.16
$SiCl_3$	119.88	84.77	119.94	84.12

Table S6 - ^{29}Si δ computed with the inclusion of scalar relativistic effects and SO correction by perturbation theory. PCM(DCM) ^{29}Si δ is also included (values in ppm)

- ## Table S7: NBO-NCS analysis

An all-electron basis set for Si (dzvp) has been used in all cases. Each σ has been calculated as the sum of the Lewis and non-Lewis contributions. For detail see the text.

SiX_3	σ Cl LP	σ expt	σ calc	σ Si-X	σ Ru-Si	σ Si-L4	σ CORE
SiH_3	0	374.88	352.92	-177.73	-96.44	-274.17	645.31

$SiMeH_2$	0	331.95	314.55	-188.15	-105.41	-293.56	626.38
$SiMe_3H$	0	304.35	284.14	-190.52	-103.89	-294.41	604.55
$SiMe_3$	0	298.64	277.15	-181.78	-104.06	-285.84	591.88
SiH_2Cl	-7.0	281.83	240.35	-220.86	-142.4	-370.26	635.45
SiHMeCl	-7.7	261.03	209.84	-221.3	-145.86	-374.86	619.85
$SiMe_2Cl$	-8.1	230.91	191.32	-216.97	-146.08	-371.15	601.53
$SiHCl_2$	-20.61	251.41	190.72	-238.19	-164.77	-423.57	641.13
$SiMeCl_2$	-24.28	226.04	171.06	-231.16	-166.61	-422.05	626.24
$SiCl_3$	-41.57	276.09	198.32	-242.18	-163.54	-447.29	657.65

Table S7 – Contributions calculated with the NBO-NCS analysis for the valence and core electrons.

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