Supplementary Material (ESI) for PCCP

Relativistic DFT calculations of the NMR properties and reactivity of transition metal methane σ-complexes: insights on C-H bond activation

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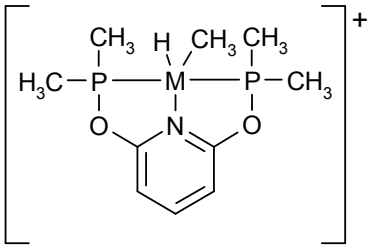
Supporting Information

L′Ir(H)CH_3^+ Model system , where L′ is the PONOP ligand with *t*-Bu groups replaced by methyl groups.

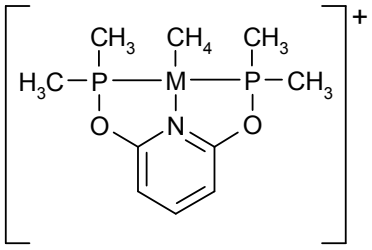
Ir	-0.068644	-4.099964	-1.664417
P	-0.058453	-2.945100	-3.698069
P	-0.080916	-4.501518	0.639527
N	-0.046452	-2.070794	-0.936194
O	-0.038048	-1.311817	-3.138283
O	-0.060754	-2.885003	1.246045
C	-0.009736	0.537765	0.000000
C	-0.013016	0.298655	-1.376955
C	-0.031229	-1.029295	-1.808835
C	-0.042666	-1.821734	0.399623
C	-0.024863	-0.522210	0.910721
C	-0.229743	-6.095203	-2.381184
C	1.498186	-2.921167	-4.814521
C	1.465326	-5.197974	1.530733
C	-1.727816	-2.932266	-4.643259
C	-1.758915	-5.087037	1.361891
H	1.652725	-6.195744	1.162308
H	-1.913452	-2.024401	-5.197984
H	-1.952621	-4.738345	2.365530
H	2.322359	-2.605744	-4.191907
H	-1.810155	-6.164956	1.318725
H	-2.503994	-4.668452	0.701555
H	2.294134	-4.561383	1.258282
H	1.370534	-5.207854	2.606520
H	-1.775900	-3.791559	-5.295718
H	-2.480297	-3.026539	-3.874309
H	1.413303	-2.244531	-5.651992
H	1.685481	-3.926169	-5.162791
H	0.203506	-6.844292	-1.710518
H	-0.001288	1.101962	-2.105110
H	-0.022462	-0.365134	1.983555
H	0.004298	1.560065	0.366895
H	-1.306091	-6.327624	-2.470155
H	0.212105	-6.248445	-3.371092
H	1.471587	-4.170018	-1.681577

L′RhCH_4^+ Model system , where L′ is the PONOP ligand with *t*-Bu groups replaced by methyl groups.

Rh	0.581491	3.914198	-1.755854
P	0.379190	2.770132	-3.777934
P	0.596572	4.426680	0.519174
O	0.187086	1.170547	-3.185831
O	0.407479	2.850042	1.170800
N	0.308567	2.030213	-1.015765
C	-0.045959	-0.558173	0.000000
C	-0.017554	-0.349029	-1.379033
C	0.159193	0.952369	-1.851056
C	0.269789	1.795165	0.335168
C	0.096435	0.519627	0.874273
C	1.115660	6.175676	-2.654683
C	-1.269018	2.965527	-4.746793
C	-0.965776	5.276370	1.247565
C	1.933752	2.484859	-4.872532
C	2.250091	4.895507	1.380722
H	-0.996127	5.302769	2.326815
H	1.883556	1.593592	-5.480417
H	-2.052598	2.810722	-4.019856
H	2.283742	4.643196	2.430297
H	2.437631	5.949955	1.241551
H	3.008667	4.324646	0.865864
H	-1.804518	4.701212	0.884101
H	-1.029319	6.277265	0.846851
H	2.096964	3.353912	-5.492619
H	2.753548	2.380519	-4.177228
H	-1.330972	3.978531	-5.116095
H	-1.394983	2.263302	-5.557602
H	-0.128423	-1.157787	-2.092605
H	0.076177	0.401362	1.951847
H	-0.181174	-1.561270	0.393537
H	1.128053	7.075778	-2.036616
H	2.036898	5.598343	-2.478723
H	1.043180	6.429002	-3.714360
H	0.137911	5.639469	-2.398511



L'Ir(H)CH_3^+



L'RhCH_4^+

Table S1 Calculated[a] chemical shifts (ppm) of the CH_4 moiety in L′Ir(H)CH_3^+ and L′RhCH_4^+ model systems

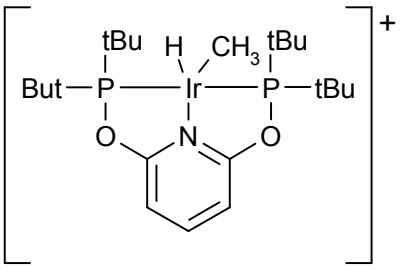
		Exp[a]	ZSO-KT2/TZ2P	ZSO-PBE0/TZ2P
L′Ir(H)CH_3^+	C	-20.6	-2.09	-11.67
	H	-41.82	-31.61	-38.99
	H_3	1.92	2.41	1.84
	H_4	-8.95[b]	-6.10	-8.37
LRhCH_4^+	C	-41.7	-43.24	-47.7
	H_4	-0.86	-1.35	-1.95

H, H_3 and H_4 refer to the hydride hydrogen, the average value of the three methyl hydrogens and the average value of the four hydrogens, respectively. [a]From Ref. 1. [b]Room temperature average.

TMS ZSO-PBE0/TZ2P//BLYP/TZ2P
Shielding Constants
C(2): 190.13 ppm
H(6): 31.35 ppm

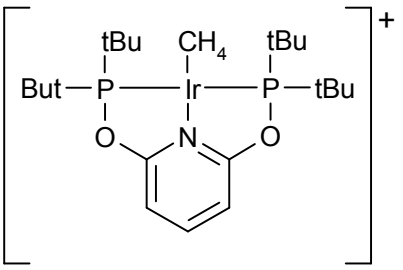
LIr(H)CH$_3^+$ optimized geometry ZSC-BLYP/TZ2P
E= -13.731048 a.u.; negative frequencies: none

Ir	-0.009736	0.537765	0.000000
P	-0.015224	0.137634	-2.304218
P	-0.015224	0.137634	2.304218
N	-0.067098	-1.617471	0.000000
O	-0.063670	-1.588178	2.329043
O	-0.063670	-1.588178	-2.329043
C	-0.087786	-2.302804	-1.173177
C	-0.087786	-2.302804	1.173177
C	-0.128564	-3.698106	-1.215259
C	-0.128564	-3.698106	1.215259
C	-0.149025	-4.387972	0.000000
C	1.663265	0.417433	3.190056
C	-1.560692	0.517439	3.370726
C	1.663265	0.417433	-3.190056
C	-1.560692	0.517439	-3.370726
C	0.185933	2.654933	0.000000
C	-1.440134	0.007597	-4.828545
C	1.758719	1.894509	-3.655021
C	2.737453	0.153656	-2.096621
C	1.919665	-0.543794	-4.377414
C	-2.761502	-0.192715	2.686671
C	-1.440134	0.007597	4.828545
C	-1.805123	2.051119	3.355329
C	1.758719	1.894509	3.655021
C	2.737453	0.153656	2.096621
C	1.919665	-0.543794	4.377414
C	-1.805123	2.051119	-3.355329
C	-2.761502	-0.192715	-2.686671
H	-0.243755	3.140573	0.882130
H	-0.143951	-4.208104	-2.171981
H	-0.143951	-4.208104	2.171981
H	-0.180778	-5.473743	0.000000
H	1.266210	2.886152	0.000000
H	-0.243755	3.140573	-0.882130
H	-1.548610	0.634617	0.000000
H	-2.728637	2.259116	-3.911821
H	-1.935795	2.434971	-2.337748
H	-0.999114	2.613029	-3.837154
H	-2.658668	-1.282357	-2.701679
H	-2.900155	0.133475	-1.650170
H	-3.673216	0.065837	-3.240499
H	-2.408099	0.154936	-5.326200
H	-0.692905	0.563496	-5.402926
H	-1.202328	-1.060590	-4.875917
H	2.784914	2.088621	-3.994946
H	1.091312	2.105179	-4.496588
H	1.539680	2.603403	-2.847381
H	2.635906	0.842952	-1.248635
H	2.704382	-0.876795	-1.724946
H	3.733796	0.315521	-2.528630
H	1.246341	-0.364434	-5.218917
H	2.945432	-0.380048	-4.735620
H	1.833417	-1.593909	-4.080391
H	-2.900155	0.133475	1.650170
H	-2.658668	-1.282357	2.701679
H	-3.673216	0.065837	3.240499
H	-0.692905	0.563496	5.402926
H	-2.408099	0.154936	5.326200
H	-1.202328	-1.060590	4.875917
H	-1.935795	2.434971	2.337748
H	-2.728637	2.259116	3.911821
H	-0.999114	2.613029	3.837154
H	1.091312	2.105179	4.496588
H	2.784914	2.088621	3.994946
H	1.539680	2.603403	2.847381
H	2.704382	-0.876795	1.724946
H	2.635906	0.842952	1.248635
H	3.733796	0.315521	2.528630
H	2.945432	-0.380048	4.735620
H	1.246341	-0.364434	5.218917
H	1.833417	-1.593909	4.080391



LIrCH$_4^+$ optimized geometry ZSC-BLYP/TZ2P
E= -13. 722816a.u.; negative frequencies: none

Ir	-0.016568	0.485784	0.000000
P	0.009634	0.149501	2.298229
P	0.009634	0.149501	-2.298229
N	-0.035778	-1.542929	0.000000
O	-0.023828	-1.567402	-2.341216
O	-0.023828	-1.567402	2.341216
C	-0.037853	-2.255539	1.176877
C	-0.037853	-2.255539	-1.176877
C	-0.053996	-3.649331	1.208604
C	-0.053996	-3.649331	-1.208604
C	-0.064639	-4.346394	0.000000
C	-1.576014	0.497318	-3.327474
C	1.652199	0.479120	-3.234436
C	-1.576014	0.497318	3.327474
C	1.652199	0.479120	3.234436
C	-0.210206	2.955344	0.000000
C	2.756433	-0.257633	2.424895
C	1.666177	-0.034534	4.695109
C	1.945007	2.004344	3.204171
C	1.945007	2.004344	-3.204171
C	2.756433	-0.257633	-2.424895
C	1.666177	-0.034534	-4.695109
C	-1.622427	1.998656	-3.715520
C	-2.766695	0.171768	-2.381266
C	-1.703503	-0.386231	-4.595881
C	-1.622427	1.998656	3.715520
C	-2.766695	0.171768	2.381266
C	-1.703503	-0.386231	4.595881
H	-0.027386	3.543798	-0.900370
H	-0.057070	-4.151224	2.169768
H	-0.057070	-4.151224	-2.169768
H	-0.078746	-5.432204	0.000000
H	-1.241408	2.587052	0.000000
H	-0.027386	3.543798	0.900370
H	0.665472	2.176112	0.000000
H	2.641779	-1.345445	2.473460
H	2.760157	0.047430	1.372612
H	3.732123	-0.004542	2.860004
H	2.691397	0.048951	5.080742
H	1.023571	0.560287	5.351512
H	1.370244	-1.086773	4.767625
H	1.200052	2.590454	3.752058
H	2.917252	2.180123	3.683301
H	2.011022	2.388031	2.179442
H	2.011022	2.388031	-2.179442
H	2.917252	2.180123	-3.683301
H	1.200052	2.590454	-3.752058
H	2.760157	0.047430	-1.372612
H	2.641779	-1.345445	-2.473460
H	3.732123	-0.004542	-2.860004
H	1.023571	0.560287	-5.351512
H	2.691397	0.048951	-5.080742
H	1.370244	-1.086773	-4.767625
H	-0.861617	2.259041	-4.458587
H	-2.602513	2.215444	-4.160710
H	-1.505747	2.660328	-2.848117
H	-2.780641	-0.885492	-2.093496
H	-2.744744	0.774000	-1.467066
H	-3.703507	0.383554	-2.913333
H	-2.698515	-0.216459	-5.029485
H	-0.965654	-0.137550	-5.361927
H	-1.620817	-1.452628	-4.362705
H	-2.602513	2.215444	4.160710
H	-0.861617	2.259041	4.458587
H	-1.505747	2.660328	2.848117
H	-2.744744	0.774000	1.467066
H	-2.780641	-0.885492	2.093496
H	-3.703507	0.383554	2.913333
H	-0.965654	-0.137550	5.361927
H	-2.698515	-0.216459	5.029485
H	-1.620817	-1.452628	4.362705

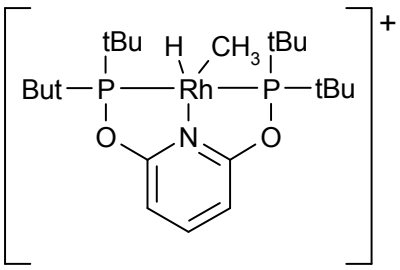


ΔE(**LIr(H)CH$_3^+$ – LIrCH$_4^+$**) = -5.2 kcal/mol
ΔG(**LIr(H)CH$_3^+$ – LIrCH$_4^+$**) = -7.8 kcal/mol

LRh(H)CH$_3^+$ optimized geometry ZSC-BLYP/TZ2P

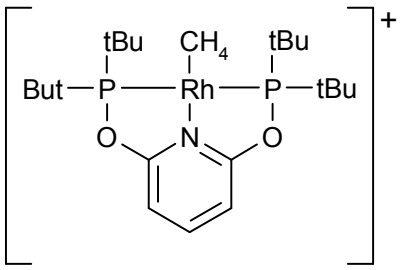
E= -13.668906 a.u.; negative frequencies: none

Rh	-0.004013	-0.647629	0.000000
P	0.035726	-0.247344	-2.312980
P	0.035726	-0.247344	2.312980
O	-0.007575	1.478673	2.327805
O	-0.007575	1.478673	-2.327805
N	-0.020922	1.507574	0.000000
C	-0.015656	2.193449	-1.171482
C	-0.015656	2.193449	1.171482
C	-0.019793	3.590094	-1.215711
C	-0.019793	3.590094	1.215711
C	-0.023543	4.279380	0.000000
C	-1.613214	-0.598744	3.230068
C	1.627833	-0.535292	3.340029
C	-1.613214	-0.598744	-3.230068
C	1.627833	-0.535292	-3.340029
C	-0.106808	-2.760333	0.000000
C	2.766962	0.228780	-2.610064
C	1.947007	-2.055171	-3.326457
C	1.524885	-0.016277	-4.795749
C	-1.659680	-2.095829	-3.634986
C	-2.714612	-0.319098	-2.167267
C	-1.866444	0.308744	-4.459559
C	1.524885	-0.016277	4.795749
C	1.947007	-2.055171	3.326457
C	-1.659680	-2.095829	3.634986
C	-2.714612	-0.319098	2.167267
C	-1.866444	0.308744	4.459559
C	2.766962	0.228780	2.610064
H	-0.017483	4.101350	-2.171913
H	-0.017483	4.101350	2.171913
H	-0.026174	5.365765	0.000000
H	0.339757	-3.223770	0.887206
H	-1.188763	-2.987912	0.000000
H	0.339757	-3.223770	-0.887206
H	1.509104	-0.827199	0.000000
H	2.901013	-2.214264	-3.846502
H	2.055655	-2.441622	-2.307003
H	1.188198	-2.650247	-3.845087
H	2.612453	1.312440	-2.627888
H	2.879811	-0.093123	-1.568751
H	3.710893	0.016288	-3.128553
H	2.515881	-0.095692	-5.263067
H	0.832308	-0.609866	-5.400113
H	1.222200	1.035762	-4.838954
H	-2.669144	-2.329823	-3.999378
H	-0.959502	-2.325697	-4.444832
H	-1.450842	-2.764402	-2.790786
H	-2.605314	-0.962405	-1.284367
H	-2.721010	0.728478	-1.845536
H	-3.697703	-0.534172	-2.606287
H	-1.190748	0.089541	-5.289983
H	-2.891400	0.129603	-4.813452
H	-1.781076	1.371595	-4.210466
H	2.879811	-0.093123	1.568751
H	2.612453	1.312440	2.627888
H	3.710893	0.016288	3.128553
H	0.832308	-0.609866	5.400113
H	2.515881	-0.095692	5.263067
H	1.222200	1.035762	4.838954
H	2.055655	-2.441622	2.307003
H	2.901013	-2.214264	3.846502
H	1.188198	-2.650247	3.845087
H	-0.959502	-2.325697	4.444832
H	-2.669144	-2.329823	3.999378
H	-1.450842	-2.764402	2.790786
H	-2.721010	0.728478	1.845536
H	-2.605314	-0.962405	1.284367
H	-3.697703	-0.534172	2.606287
H	-2.891400	0.129603	4.813452
H	-1.190748	0.089541	5.289983
H	-1.781076	1.371595	4.210466



$LRhCH_4^+$ optimized geometry ZSC-BLYP/TZ2P
E= -13.680964 a.u.; negative frequencies: none

Rh	-0.045959	-0.558173	0.000000
P	0.001523	-0.208561	-2.305241
P	0.001523	-0.208561	2.305241
O	-0.036975	1.507149	2.337173
O	-0.036975	1.507149	-2.337173
N	-0.045295	1.484281	0.000000
C	-0.046073	2.195789	-1.172829
C	-0.046073	2.195789	1.172829
C	-0.057103	3.590875	-1.208816
C	-0.057103	3.590875	1.208816
C	-0.064613	4.287286	0.000000
C	-1.572918	-0.549269	3.354642
C	1.665052	-0.520163	3.215753
C	-1.572918	-0.549269	-3.354642
C	1.665052	-0.520163	-3.215753
C	-0.251195	-3.041193	0.000000
C	2.745649	0.214983	2.373652
C	1.961438	-2.044370	3.191523
C	1.961438	-2.044370	-3.191523
C	1.706656	0.011279	-4.669110
C	2.745649	0.214983	-2.373652
C	1.706656	0.011279	4.669110
C	-1.624649	-2.054512	3.725158
C	-2.767311	-0.205203	2.419700
C	-1.678546	0.324231	4.630872
C	-1.624649	-2.054512	-3.725158
C	-2.767311	-0.205203	-2.419700
C	-1.678546	0.324231	-4.630872
H	-0.058507	4.093134	-2.169700
H	-0.058507	4.093134	2.169700
H	-0.074254	5.373226	0.000000
H	-0.138976	-3.649193	0.900048
H	-1.245545	-2.567672	0.000000
H	-0.138976	-3.649193	-0.900048
H	0.639821	-2.323402	0.000000
H	2.624669	1.302743	-2.411559
H	2.730980	-0.101379	-1.324099
H	3.733742	-0.024831	-2.788122
H	2.739821	-0.062178	-5.036368
H	1.079569	-0.577034	-5.346261
H	1.407546	1.063398	-4.734291
H	1.237549	-2.626100	-3.771933
H	2.950839	-2.215156	-3.636682
H	1.990506	-2.440496	-2.169428
H	1.990506	-2.440496	2.169428
H	2.950839	-2.215156	3.636682
H	1.237549	-2.626100	3.771933
H	2.730980	-0.101379	1.324099
H	2.624669	1.302743	2.411559
H	3.733742	-0.024831	2.788122
H	1.079569	-0.577034	5.346261
H	2.739821	-0.062178	5.036368
H	1.407546	1.063398	4.734291
H	-0.855666	-2.329592	4.454814
H	-2.600142	-2.272659	4.180271
H	-1.523187	-2.705969	2.847757
H	-2.778737	0.855843	2.145785
H	-2.755065	-0.796292	1.497116
H	-3.703610	-0.419615	2.951908
H	-2.671933	0.165665	5.073248
H	-0.936870	0.059049	5.388113
H	-1.583061	1.391682	4.406199
H	-2.600142	-2.272659	-4.180271
H	-0.855666	-2.329592	-4.454814
H	-1.523187	-2.705969	-2.847757
H	-2.755065	-0.796292	-1.497116
H	-2.778737	0.855843	-2.145785
H	-3.703610	-0.419615	-2.951908
H	-0.936870	0.059049	-5.388113
H	-2.671933	0.165665	-5.073248
H	-1.583061	1.391682	-4.406199



$\Delta E(\mathbf{LRh(H)CH_3^+} - \mathbf{LRhCH_4^+}) = +7.6$ kcal/mol
$\Delta G(\mathbf{LRh(H)CH_3^+} - \mathbf{LRhCH_4^+}) = +4.8$ kcal/mol

LIrCH$_3$ optimized geometry ZSC-BLYP/TZ2P
E= -13.77607872 a.u.; negative frequencies: none

Ir	-0.603926	-0.034409	0.000000
P	-0.230622	-0.001660	2.243344
P	-0.230622	-0.001660	-2.243344
O	1.504688	-0.083021	-2.330925
O	1.504688	-0.083021	2.330925
N	1.504840	-0.074589	0.000000
C	2.210982	-0.106222	1.169913
C	2.210982	-0.106222	-1.169913
C	3.605526	-0.164057	1.210499
C	3.605526	-0.164057	-1.210499
C	4.305840	-0.193222	0.000000
C	-0.614172	-1.557853	-3.323861
C	-0.482067	1.652612	-3.212666
C	-0.614172	-1.557853	3.323861
C	-0.482067	1.652612	3.212666
C	-2.742067	-0.114717	0.000000
C	0.267078	2.731000	-2.381345
C	-1.994730	2.000502	-3.215621
C	-1.994730	2.000502	3.215621
C	0.067427	1.664648	4.659012
C	0.267078	2.731000	2.381345
C	0.067427	1.664648	-4.659012
C	-2.119772	-1.552947	-3.697173
C	-0.328961	-2.770328	-2.393131
C	0.254528	-1.709147	-4.597791
C	-2.119772	-1.552947	3.697173
C	-0.328961	-2.770328	2.393131
C	0.254528	-1.709147	4.597791
H	4.108016	-0.186498	2.171605
H	4.108016	-0.186498	-2.171605
H	5.391131	-0.239649	0.000000
H	-3.213874	0.344411	-0.879851
H	-3.050750	-1.175895	0.000000
H	-3.213874	0.344411	0.879851
H	1.352029	2.580893	2.403953
H	-0.061013	2.723603	1.335896
H	0.053037	3.720222	2.811132
H	0.031729	2.695480	5.042287
H	-0.532610	1.047551	5.336132
H	1.109408	1.328300	4.707080
H	-2.587799	1.294631	3.807212
H	-2.127376	2.997441	3.660989
H	-2.402705	2.026296	2.199322
H	-2.402705	2.026296	-2.199322
H	-2.127376	2.997441	-3.660989
H	-2.587799	1.294631	-3.807212
H	-0.061013	2.723603	-1.335896
H	1.352029	2.580893	-2.403953
H	0.053037	3.720222	-2.811132
H	-0.532610	1.047551	-5.336132
H	0.031729	2.695480	-5.042287
H	1.109408	1.328300	-4.707080
H	-2.357637	-0.784983	-4.441914
H	-2.383105	-2.526855	-4.134942
H	-2.759781	-1.398170	-2.820001
H	0.730900	-2.827776	-2.119603
H	-0.912350	-2.715661	-1.468453
H	-0.590675	-3.696097	-2.926347
H	0.060849	-2.699016	-5.037576
H	0.021607	-0.961485	-5.360656
H	1.323949	-1.649568	-4.368333
H	-2.383105	-2.526855	4.134942
H	-2.357637	-0.784983	4.441914
H	-2.759781	-1.398170	2.820001
H	-0.912350	-2.715661	1.468453
H	0.730900	-2.827776	2.119603
H	-0.590675	-3.696097	2.926347
H	0.021607	-0.961485	5.360656
H	0.060849	-2.699016	5.037576
H	1.323949	-1.649568	4.368333

LRhCH$_3$ optimized geometry ZSC-BLYP/TZ2P
E= -13.72124702 a.u.; negative frequencies: none

Rh	-0.614561	-0.041501	0.000000
P	-0.248229	0.004180	2.251718
P	-0.248229	0.004180	-2.251718
O	1.493177	-0.083782	-2.327609
O	1.493177	-0.083782	2.327609
N	1.497560	-0.078321	0.000000
C	2.198579	-0.108815	1.168215
C	2.198579	-0.108815	-1.168215
C	3.594996	-0.168153	1.211522
C	3.594996	-0.168153	-1.211522
C	4.292486	-0.198463	0.000000
C	-0.611618	-1.545188	-3.351332
C	-0.469504	1.670066	-3.213887
C	-0.611618	-1.545188	3.351332
C	-0.469504	1.670066	3.213887
C	-2.752584	-0.142698	0.000000
C	0.263640	2.733509	-2.349307
C	-1.981731	2.018926	-3.242766
C	-1.981731	2.018926	3.242766
C	0.113804	1.702120	4.646387
C	0.263640	2.733509	2.349307
C	0.113804	1.702120	-4.646387
C	-2.121835	-1.557997	-3.705726
C	-0.299381	-2.758974	-2.430477
C	0.245846	-1.674539	-4.634603
C	-2.121835	-1.557997	3.705726
C	-0.299381	-2.758974	2.430477
C	0.245846	-1.674539	4.634603
H	4.099308	-0.190549	2.171597
H	4.099308	-0.190549	-2.171597
H	5.377947	-0.246523	0.000000
H	-3.222613	0.312059	-0.884528
H	-3.028236	-1.213433	0.000000
H	-3.222613	0.312059	0.884528
H	1.348837	2.582729	2.353145
H	-0.084295	2.710902	1.309828
H	0.059608	3.730864	2.764919
H	0.093880	2.738862	5.015302
H	-0.472738	1.098571	5.347152
H	1.154735	1.359810	4.674257
H	-2.560182	1.326715	3.864714
H	-2.106544	3.026326	3.666401
H	-2.413308	2.019634	2.235556
H	-2.413308	2.019634	-2.235556
H	-2.106544	3.026326	-3.666401
H	-2.560182	1.326715	-3.864714
H	-0.084295	2.710902	-1.309828
H	1.348837	2.582729	-2.353145
H	0.059608	3.730864	-2.764919
H	-0.472738	1.098571	-5.347152
H	0.093880	2.738862	-5.015302
H	1.154735	1.359810	-4.674257
H	-2.380148	-0.784454	-4.438086
H	-2.378184	-2.530355	-4.151273
H	-2.752300	-1.421712	-2.818391
H	0.766218	-2.809506	-2.178019
H	-0.866828	-2.714098	-1.494422
H	-0.563909	-3.685794	-2.960318
H	0.070001	-2.667020	-5.076438
H	-0.012103	-0.929554	-5.392376
H	1.316417	-1.591991	-4.416784
H	-2.378184	-2.530355	4.151273
H	-2.380148	-0.784454	4.438086
H	-2.752300	-1.421712	2.818391
H	-0.866828	-2.714098	1.494422
H	0.766218	-2.809506	2.178019
H	-0.563909	-3.685794	2.960318
H	-0.012103	-0.929554	5.392376
H	0.070001	-2.667020	5.076438
H	1.316417	-1.591991	4.416784

LIr+ optimized geometry ZSC-BLYP/TZ2P
E= -12.85047644 a.u.; negative frequencies: none

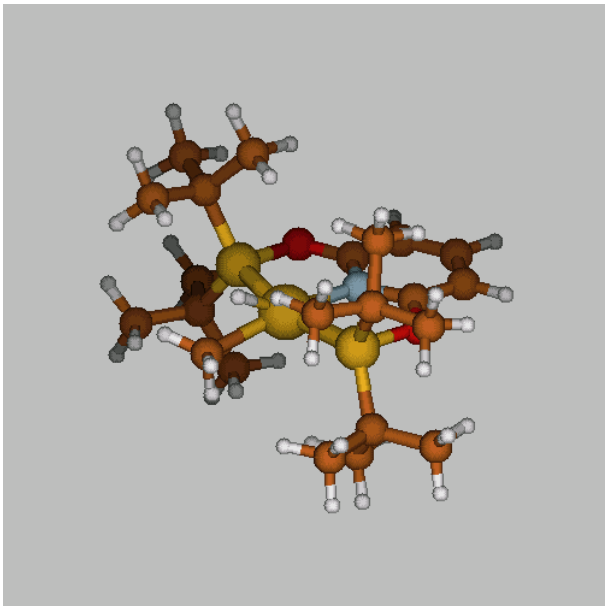
C	0.005084	0.452683	0.000000
C	0.052884	-0.242683	1.208197
C	0.151488	-1.632437	1.185385
N	0.206542	-2.341130	0.000000
C	0.151488	-1.632437	-1.185385
C	0.052884	-0.242683	-1.208197
Ir	0.348527	-4.308811	0.000000
P	0.314803	-4.030848	-2.298103
C	-1.284170	-4.551920	-3.211689
C	-1.333458	-4.172048	-4.710657
O	0.197114	-2.315393	2.350550
P	0.314803	-4.030848	2.298103
C	-1.284170	-4.551920	3.211689
C	-1.431815	-6.089681	3.037628
O	0.197114	-2.315393	-2.350550
C	1.929832	-4.267979	3.301213
C	1.983838	-3.429762	4.603880
C	1.929832	-4.267979	-3.301213
C	1.983838	-3.429762	-4.603880
C	2.104841	-5.777261	-3.615500
C	3.076923	-3.802509	-2.360614
C	-1.431815	-6.089681	-3.037628
C	-2.450956	-3.848103	-2.464297
C	2.104841	-5.777261	3.615500
C	3.076923	-3.802509	2.360614
C	-2.450956	-3.848103	2.464297
C	-1.333458	-4.172048	4.710657
H	0.015321	0.257115	2.169787
H	0.015321	0.257115	-2.169787
H	-0.071188	1.535626	0.000000
H	-2.429564	-2.762148	2.603026
H	-2.434314	-4.066195	1.390467
H	-3.399086	-4.219607	2.874451
H	-2.338859	-4.395872	5.092615
H	-0.623089	-4.749095	5.310655
H	-1.149160	-3.104303	4.873741
H	-0.647859	-6.652200	3.554798
H	-2.395484	-6.398895	3.463965
H	-1.431881	-6.381131	1.978933
H	-1.431881	-6.381131	-1.978933
H	-2.395484	-6.398895	-3.463965
H	-0.647859	-6.652200	-3.554798
H	-2.434314	-4.066195	-1.390467
H	-2.429564	-2.762148	-2.603026
H	-3.399086	-4.219607	-2.874451
H	-0.623089	-4.749095	-5.310655
H	-2.338859	-4.395872	-5.092615
H	-1.149160	-3.104303	-4.873741
H	1.378949	-6.135932	-4.352476
H	3.106181	-5.934214	-4.037784
H	2.029167	-6.402456	-2.715899
H	3.001598	-2.735704	-2.121934
H	3.089486	-4.364596	-1.420721
H	4.034485	-3.960618	-2.874064
H	2.992638	-3.523304	-5.028672
H	1.276217	-3.775315	-5.360832
H	1.802430	-2.366614	-4.413867
H	3.106181	-5.934214	4.037784
H	1.378949	-6.135932	4.352476
H	2.029167	-6.402456	2.715899
H	3.089486	-4.364596	1.420721
H	3.001598	-2.735704	2.121934
H	4.034485	-3.960618	2.874064
H	1.276217	-3.775315	5.360832
H	2.992638	-3.523304	5.028672
H	1.802430	-2.366614	4.413867

LRh+ optimized geometry ZSC-BLYP/TZ2P
E= -12.81379010 a.u.; negative frequencies: none

C	-0.030832	-0.541075	0.000000
C	0.057674	0.149427	-1.208918
C	0.238611	1.532397	-1.177909
N	0.335361	2.235261	0.000000
C	0.238611	1.532397	1.177909
C	0.057674	0.149427	1.208918
Rh	0.604577	4.228206	0.000000
O	0.325925	2.214121	-2.343440
P	0.531694	3.918441	-2.297977
C	-1.055012	4.518463	-3.186620
C	-2.243425	3.857185	-2.433644
O	0.325925	2.214121	2.343440
P	0.531694	3.918441	2.297977
C	-1.055012	4.518463	3.186620
C	-1.142266	4.163011	4.689520
C	2.140614	4.065274	-3.327445
C	2.139991	3.208055	-4.618649
C	2.140614	4.065274	3.327445
C	2.139991	3.208055	4.618649
C	2.383144	5.560869	3.662180
C	3.273873	3.557531	2.390606
C	-2.243425	3.857185	2.433644
C	-1.127317	6.058795	2.984479
C	2.383144	5.560869	-3.662180
C	3.273873	3.557531	-2.390606
C	-1.127317	6.058795	-2.984479
C	-1.142266	4.163011	-4.689520
H	-0.009318	-0.348348	-2.169889
H	-0.009318	-0.348348	2.169889
H	-0.170733	-1.617946	0.000000
H	-2.275568	2.774123	-2.591480
H	-2.202352	4.052868	-1.355491
H	-3.179859	4.280282	-2.820208
H	-2.138056	4.446135	-5.058145
H	-0.406895	4.706654	-5.291071
H	-1.018939	3.088552	-4.866601
H	-0.320848	6.592258	-3.498358
H	-2.078354	6.424154	-3.394366
H	-1.102354	6.329987	-1.920526
H	-1.102354	6.329987	1.920526
H	-2.078354	6.424154	3.394366
H	-0.320848	6.592258	3.498358
H	-2.202352	4.052868	1.355491
H	-2.275568	2.774123	2.591480
H	-3.179859	4.280282	2.820208
H	-0.406895	4.706654	5.291071
H	-2.138056	4.446135	5.058145
H	-1.018939	3.088552	4.866601
H	1.662758	5.946612	4.391214
H	3.383701	5.666130	4.102239
H	2.352093	6.198751	2.768456
H	3.149459	2.498963	2.136030
H	3.324108	4.130963	1.457560
H	4.234659	3.662935	2.911594
H	3.145211	3.252087	5.060303
H	1.435064	3.572979	5.369469
H	1.916006	2.156506	4.410260
H	3.383701	5.666130	-4.102239
H	1.662758	5.946612	-4.391214
H	2.352093	6.198751	-2.768456
H	3.324108	4.130963	-1.457560
H	3.149459	2.498963	-2.136030
H	4.234659	3.662935	-2.911594
H	1.435064	3.572979	-5.369469
H	3.145211	3.252087	-5.060303
H	1.916006	2.156506	-4.410260

TS [**$LIrCH_4^+$-$LIr(H)CH_3^+$**] optimized geometry
ZSC-BLYP/TZ2P
E= -13.717056 a.u.; one negative frequency: -712.7 cm^{-1}.

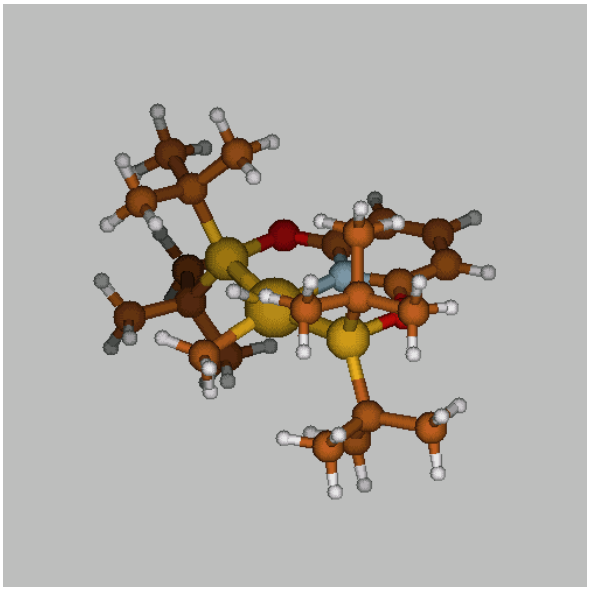
Ir	-0.514979	-0.017960	-0.000046
P	-0.155766	0.019086	2.300933
P	-0.155995	0.018298	-2.300861
O	1.570643	-0.030595	-2.336792
O	1.571019	-0.026165	2.336721
N	1.565843	-0.059153	-0.000018
C	2.266179	-0.062721	1.178303
C	2.265982	-0.064639	-1.178456
C	3.661144	-0.095903	1.212512
C	3.660925	-0.097547	-1.212937
C	4.352268	-0.115959	-0.000280
C	-0.500740	-1.567308	-3.332036
C	-0.464028	1.664727	-3.235076
C	-0.497864	-1.567211	3.331878
C	-0.467193	1.664633	3.235543
C	-2.744763	-0.377620	0.000036
C	0.274786	2.763557	2.424691
C	-1.991544	1.962320	3.208371
C	0.051189	1.674584	4.694111
C	-1.995608	-1.605412	3.734265
C	-0.188773	-2.755879	2.377842
C	0.398345	-1.702889	4.589676
C	0.055408	1.675004	-4.693333
C	-1.988034	1.964846	-3.209153
C	-1.998413	-1.603376	-3.734997
C	-0.194013	-2.756531	-2.377936
C	0.395558	-1.704169	-4.589608
C	0.279105	2.761897	-2.422921
H	4.168601	-0.100980	2.170580
H	4.168224	-0.104271	-2.171106
H	5.438227	-0.140653	-0.000447
H	-3.307894	-0.090403	-0.890427
H	-2.604951	-1.464190	0.002430
H	-3.309681	-0.087159	0.888394
H	-1.878993	0.834252	-0.000137
H	-2.162249	2.936045	3.686482
H	-2.378468	2.026174	2.184814
H	-2.578665	1.220524	3.759238
H	1.361990	2.640982	2.469751
H	-0.034045	2.771629	1.373935
H	0.030661	3.740652	2.861797
H	-0.029596	2.699081	5.082243
H	-0.542749	1.031718	5.350909
H	1.103193	1.377039	4.763112
H	-2.212868	-2.584893	4.180921
H	-2.243163	-0.844693	4.481765
H	-2.665454	-1.483311	2.874500
H	-0.804428	-2.729485	1.472819
H	0.865313	-2.775865	2.078406
H	-0.398862	-3.694123	2.908106
H	0.162750	-0.964373	5.359259
H	0.225819	-2.697096	5.024376
H	1.462895	-1.627320	4.345963
H	-0.028292	2.767893	-1.371710
H	1.366216	2.639113	-2.469736
H	0.034595	3.739940	-2.857693
H	-0.540223	1.035208	-5.351680
H	-0.021861	2.700380	-5.079914
H	1.106497	1.374127	-4.762126
H	-2.375091	2.031117	-2.185825
H	-2.157087	2.937943	-3.689179
H	-2.576199	1.223005	-3.758917
H	-2.244422	-0.843253	-4.483675
H	-2.217106	-2.583067	-4.180512
H	-2.668387	-1.479084	-2.875660
H	0.859047	-2.776254	-2.074929
H	-0.812842	-2.731238	-1.475063
H	-0.401802	-3.694505	-2.909608
H	0.214803	-2.694645	-5.029401
H	0.167460	-0.959815	-5.355779
H	1.460425	-1.639191	-4.344268



Structure of the transition state of **$LIrCH_4^+$-$LIr(H)CH_3^+$**
Image produced with MOLDEN: G.Schaftenaar and J.H. Noordik, "Molden: a pre- and post-processing program for molecular and electronic structures", J. Comput.-Aided Mol. Design, 14 (2000) 123-134

TS [**$LRhCH_4^+$-$LRh(H)CH_3^+$**] optimized geometry ZSC-BLYP/TZ2P
E= -13.62489 a.u.; one negative frequency: -631.6 cm^{-1}.

Rh	-0.607364	-0.068670	0.000303
P	-0.226423	0.020864	2.311272
P	-0.226084	0.020994	-2.311612
O	1.498934	-0.085809	-2.331017
O	1.498661	-0.086536	2.331181
N	1.503728	-0.124800	0.000105
C	2.198697	-0.134632	1.174533
C	2.198821	-0.134305	-1.174229
C	3.593961	-0.187750	1.214138
C	3.594091	-0.187487	-1.213675
C	4.283481	-0.219423	0.000282
C	-0.604023	-1.523162	-3.390278
C	-0.468234	1.709199	-3.191869
C	-0.604539	-1.523305	3.390356
C	-0.468303	1.708918	3.191057
C	-2.760448	-0.431602	0.000419
C	0.310238	2.748133	2.336685
C	-1.981249	2.059845	3.157589
C	0.060813	1.748601	4.645344
C	-2.097844	-1.498215	3.809435
C	-0.347894	-2.740426	2.456198
C	0.305522	-1.656965	4.638023
C	0.062109	1.748930	-4.645756
C	-1.981237	2.059445	-3.159460
C	-2.097176	-1.497079	-3.810275
C	-0.348797	-2.740320	-2.455747
C	0.306473	-1.657935	-4.637522
C	0.309335	2.748698	-2.336924
H	4.102972	-0.197541	2.171304
H	4.103167	-0.197201	-2.170802
H	5.368965	-0.261726	0.000388
H	-3.316074	-0.120931	-0.888323
H	-2.650202	-1.526096	-0.002649
H	-3.313726	-0.125348	0.892084
H	-1.786427	0.947515	0.001235
H	-2.114660	3.062389	3.585499
H	-2.373641	2.082783	2.134306
H	-2.589052	1.367612	3.749432
H	1.392269	2.585409	2.379699
H	-0.005797	2.733442	1.287879
H	0.107418	3.749501	2.738459
H	0.014731	2.786612	5.002508
H	-0.546799	1.144087	5.325913
H	1.104011	1.420986	4.715226
H	-2.346120	-2.458468	4.281167
H	-2.308758	-0.711160	4.541108
H	-2.771760	-1.371180	2.953285
H	-0.987148	-2.720577	1.566783
H	0.698240	-2.794515	2.133373
H	-0.568859	-3.662258	3.010180
H	0.116576	-0.881905	5.384577
H	0.096698	-2.627087	5.109961
H	1.367898	-1.637247	4.374365
H	-0.008744	2.735540	-1.288748
H	1.391347	2.585213	-2.377587
H	0.108120	3.749704	-2.740375
H	-0.545414	1.145088	-5.327040
H	0.017200	2.787090	-5.002634
H	1.105103	1.420567	-4.714967
H	-2.374910	2.079989	-2.136587
H	-2.114605	3.062915	-3.585230
H	-2.587957	1.368256	-3.753603
H	-2.306396	-0.711582	-4.544102
H	-2.346525	-2.458185	-4.279680
H	-2.771445	-1.366791	-2.954907
H	0.696576	-2.793908	-2.130356
H	-0.990236	-2.721089	-1.567915
H	-0.567842	-3.662168	-3.010459
H	0.094222	-2.626254	-5.111620
H	0.121342	-0.880661	-5.382695
H	1.368748	-1.643155	-4.373088



Structure of the transition state of **$LRhCH_4^+$-$LRh(H)CH_3^+$**
Image produced with MOLDEN: G.Schaftenaar and J.H. Noordik, "Molden: a pre- and post-processing program for molecular and electronic structures", J. Comput.-Aided Mol. Design, 14 (2000) 123-134

CH_5^+ optimized geometry ZSC-BLYP/TZ2P

C	-0.115867	0.097704	-0.159446
H	-0.126283	0.319077	0.912359
H	0.956824	0.079332	-0.477958
H	-0.573323	-0.825340	-0.529244
H	-0.010984	1.007015	-0.913312
H	-0.949385	0.856916	-0.504474

Calculated NMR parameters

Only the isotropic averages of the shielding tensor σ and of the scalar coupling tensor **J** are reported.
Atom numbering is the same as in the structures reported above
k: reduced coupling constant,
j: *J* coupling constant in Hz.

TMS ZSC-KT2/TZ2P//BLYP/TZ2P
Shielding Constants

```
C(2): 190.53 ppm
H(6): 31.33 ppm
```

TMS ZSO-KT2/TZ2P//BLYP/TZ2P
Shielding Constants

```
C(2): 191.44 ppm
H(6): 31.34 ppm
```

$LIrCH_4^+$ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Ir(1): 396.73 ppm
P(2): 134.48 ppm
P(3): 134.48 ppm
C(16): 212.58 ppm
H(29): 31.46 ppm
H(33): 27.41 ppm
H(34): 31.46 ppm
H(35): 35.63 ppm
```

Coupling Constants

```
C(16)-H(29) k=51.653    j=156.046
C(16)-H(33) k=42.150    j=127.335
C(16)-H(34) k=51.653    j=156.046
C(16)-H(35) k=22.605    j=68.289
C(16)-Ir(1) k=-331.339  j=0.000
C(16)-P(2) k=0.365      j=0.447
Ir(1)-P(2) k=1603.549   j=0.000
Ir(1)-H(29) k=24.645    j=0.000
Ir(1)-H(33) k=18.653    j=0.000
Ir(1)-H(34) k=24.645    j=0.000
Ir(1)-H(35) k=161.143   j=0.000
P(2)-H(29) k=0.782      j=3.805
P(2)-H(33) k=-0.033     j=-0.162
P(2)-H(34) k=0.553      j=2.693
P(2)-H(35) k=-0.198     j=-0.965
```

$LIrCH_4^+$ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Ir(1): 2979.29 ppm
P(2): 151.98 ppm
P(3): 151.98 ppm
C(16): 236.62 ppm
H(29): 31.24 ppm
H(33): 27.61 ppm
H(34): 31.24 ppm
H(35): 37.68 ppm
```

Coupling Constants

```
C(16)-H(29) k=51.655    j=156.051
C(16)-H(33) k=42.353    j=127.949
C(16)-H(34) k=51.655    j=156.051
C(16)-H(35) k=22.701    j=68.579
C(16)-Ir(1) k=-334.260  j=0.000
C(16)-P(2) k=0.245      j=0.300
Ir(1)-P(2) k=1587.045   j=0.000
Ir(1)-H(29) k=22.416    j=0.000
Ir(1)-H(33) k=17.363    j=0.000
Ir(1)-H(34) k=22.416    j=0.000
Ir(1)-H(35) k=155.261   j=0.000
P(2)-H(29) k=0.795      j=3.869
P(2)-H(33) k=-0.035     j=-0.172
P(2)-H(34) k=0.501      j=2.436
P(2)-H(35) k=-0.205     j=-0.997
```

LIr(H)CH_3^+ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P
LIr(H)CH_3^+ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Ir(1): -815.15 ppm
P(2): 139.95 ppm
P(3): 139.95 ppm
C(16): 174.17 ppm
H(29): 29.41 ppm
H(33): 30.47 ppm
H(34): 29.41 ppm
H(35): 42.94 ppm
```

Coupling Constants

```
C(16)-H(29) k=46.295    j=139.858
C(16)-H(33) k=42.748    j=129.144
C(16)-H(34) k=46.295    j=139.858
C(16)-H(35) k=-0.733    j=-2.216
C(16)-Ir(1) k=614.855   j=0.000
C(16)-P(2) k=-1.046     j=-1.280
Ir(1)-P(2) k=1144.691   j=0.000
Ir(1)-H(29) k=8.642     j=0.000
Ir(1)-H(33) k=-36.070   j=0.000
Ir(1)-H(34) k=8.642     j=0.000
Ir(1)-H(35) k=674.310   j=0.000
P(2)-H(29) k=0.723      j=3.520
P(2)-H(33) k=-0.150     j=-0.732
P(2)-H(34) k=2.140      j=10.418
P(2)-H(35) k=-1.622     j=-7.896
```

LIr(H)CH_3^+ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P
LIr(H)CH_3^+ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Ir(1): 1715.90 ppm
P(2): 154.69 ppm
P(3): 154.69 ppm
C(16): 193.17 ppm
H(29): 28.48 ppm
H(33): 29.07 ppm
H(34): 28.48 ppm
H(35): 62.68 ppm
```

Coupling Constants

```
C(16)-H(29) k=46.389    j=140.142
C(16)-H(33) k=42.677    j=128.930
C(16)-H(34) k=46.389    j=140.142
C(16)-H(35) k=-0.686    j=-2.072
C(16)-Ir(1) k=629.057   j=0.000
C(16)-P(2) k=-1.388     j=-1.699
Ir(1)-P(2) k=1114.872   j=0.000
Ir(1)-H(29) k=6.797     j=0.000
Ir(1)-H(33) k=-38.471   j=0.000
Ir(1)-H(34) k=6.797     j=0.000
Ir(1)-H(35) k=722.791   j=0.000
P(2)-H(29) k=0.712      j=3.465
P(2)-H(33) k=-0.164     j=-0.801
P(2)-H(34) k=2.088      j=10.166
P(2)-H(35) k=-1.510     j=-7.349
```

$LIrCH_3$ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P
$LIrCH_3$ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Ir(1): 219.68 ppm
P(2): 152.83 ppm
P(3): 152.83 ppm
C(16): 187.18 ppm
H(32): 30.66 ppm
H(33): 31.33 ppm
H(34): 30.66 ppm
```

Coupling Constants

```
C(16)-H(32) k=43.594 j=131.700
C(16)-H(33) k=42.541 j=128.518
C(16)-H(34) k=43.594 j=131.700
C(16)-Ir(1) k=626.197 j=0.000
C(16)-P(2) k=-1.579 j=-1.933
Ir(1)-P(2) k=1947.891 j=0.000
Ir(1)-H(32) k=-9.736 j=0.000
Ir(1)-H(33) k=-17.723 j=0.000
Ir(1)-H(34) k=-9.736 j=0.000
P(2)-H(32) k=0.983 j=4.783
P(2)-H(33) k=-0.102 j=-0.495
P(2)-H(34) k=2.095 j=10.198
```

$LIrCH_3$ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Ir(1): 2507.29 ppm
P(2): 164.26 ppm
P(3): 164.26 ppm
C(16): 206.74 ppm
H(32): 29.56 ppm
H(33): 29.43 ppm
H(34): 29.56 ppm
```

Coupling Constants

```
C(16)-H(32) k=43.677 j=131.950
C(16)-H(33) k=42.486 j=128.353
C(16)-H(34) k=43.677 j=131.950
C(16)-Ir(1) k=643.241 j=0.000
C(16)-P(2) k=-2.008 j=-2.458
Ir(1)-P(2) k=1920.193 j=0.000
Ir(1)-H(32) k=-11.814 j=0.000
Ir(1)-H(33) k=-21.483 j=0.000
Ir(1)-H(34) k=-11.814 j=0.000
P(2)-H(32) k=0.970 j=4.724
P(2)-H(33) k=-0.140 j=-0.681
P(2)-H(34) k=2.039 j=9.925
```

$LRhCH_4^+$ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Rh(1): -1542.22 ppm
P(2): 104.93 ppm
P(3): 104.93 ppm
C(16): 219.49 ppm
H(32): 31.91 ppm
H(33): 28.69 ppm
H(34): 31.91 ppm
H(35): 35.17 ppm
```

Coupling Constants

```
C(16)-H(32) k=51.204    j=154.691
C(16)-H(33) k=38.726    j=116.993
C(16)-H(34) k=51.204    j=154.691
C(16)-H(35) k=25.605    j=77.353
C(16)-Rh(1) k=-44.590   j=4.260
C(16)-P(2) k=-0.028     j=-0.035
Rh(1)-P(2) k=589.326    j=-90.718
Rh(1)-H(32) k=10.743    j=-4.081
Rh(1)-H(33) k=13.789    j=-5.238
Rh(1)-H(34) k=10.743    j=-4.081
Rh(1)-H(35) k=47.107    j=-17.894
P(2)-H(32) k=0.496      j=2.415
P(2)-H(33) k=-0.093     j=-0.454
P(2)-H(34) k=0.845      j=4.114
P(2)-H(35) k=-0.272     j=-1.326
```

$LRhCH_4^+$ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P
$LRhCH_4^+$ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Rh(1): -1047.72 ppm
P(2): 128.98 ppm
P(3): 128.98 ppm
C(16): 229.47 ppm
H(32): 31.98 ppm
H(33): 29.00 ppm
H(34): 31.98 ppm
H(35): 36.30 ppm
```

Coupling Constants

```
C(16)-H(32) k=51.212    j=154.713
C(16)-H(33) k=38.770    j=117.124
C(16)-H(34) k=51.212    j=154.713
C(16)-H(35) k=25.629    j=77.425
C(16)-Rh(1) k=-40.499   j=3.869
C(16)-P(2) k=-0.116     j=-0.142
Rh(1)-P(2) k=602.932    j=-92.812
Rh(1)-H(32) k=10.537    j=-4.003
Rh(1)-H(33) k=13.730    j=-5.215
Rh(1)-H(34) k=10.537    j=-4.003
Rh(1)-H(35) k=46.997    j=-17.852
P(2)-H(32) k=0.494      j=2.404
P(2)-H(33) k=-0.098     j=-0.479
P(2)-H(34) k=0.834      j=4.060
P(2)-H(35) k=-0.292     j=-1.421
```

$LRh(H)CH_3^+$ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P
$LRh(H)CH_3^+$ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

Rh(1): -1534.11 ppm
P(2): 121.06 ppm
P(3): 121.06 ppm
C(16): 172.63 ppm
H(32): 29.44 ppm
H(33): 30.26 ppm
H(34): 29.44 ppm
H(35): 41.00 ppm

Couping Constants

C(16)-H(32)	k=47.956	j=144.876
C(16)-H(33)	k=44.077	j=133.159
C(16)-H(34)	k=47.956	j=144.876
C(16)-H(35)	k=-0.854	j=-2.581
C(16)-Rh(1)	k=181.605	j=-17.350
C(16)-P(2)	k=-2.091	j=-2.560
Rh(1)-P(2)	k=474.991	j=-73.117
Rh(1)-H(32)	k=1.727	j=-0.656
Rh(1)-H(33)	k=-10.635	j=4.040
Rh(1)-H(34)	k=1.727	j=-0.656
Rh(1)-H(35)	k=172.521	j=-65.533
P(2)-H(32)	k=0.294	j=1.431
P(2)-H(33)	k=-0.114	j=-0.555
P(2)-H(34)	k=2.892	j=14.078
P(2)-H(35)	k=-1.498	j=-7.293

$LRh(H)CH_3^+$ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P
$LRh(H)CH_3^+$ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

Rh(1): -1109.38 ppm
P(2): 141.02 ppm
P(3): 141.02 ppm
C(16): 183.20 ppm
H(32): 29.40 ppm
H(33): 30.28 ppm
H(34): 29.40 ppm
H(35): 49.76 ppm

Coupling Constants

C(16)-H(32)	k=48.005	j=145.024
C(16)-H(33)	k=44.084	j=133.178
C(16)-H(34)	k=48.005	j=145.024
C(16)-H(35)	k=-0.868	j=-2.623
C(16)-Rh(1)	k=190.346	j=-18.185
C(16)-P(2)	k=-2.204	j=-2.698
Rh(1)-P(2)	k=483.513	j=-74.429
Rh(1)-H(32)	k=1.248	j=-0.474
Rh(1)-H(33)	k=-10.894	j=4.138
Rh(1)-H(34)	k=1.248	j=-0.474
Rh(1)-H(35)	k=185.777	j=-70.569
P(2)-H(32)	k=0.287	j=1.398
P(2)-H(33)	k=-0.113	j=-0.548
P(2)-H(34)	k=2.886	j=14.047
P(2)-H(35)	k=-1.463	j=-7.120

$LRhCH_3$ ZSC-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Rh(1): -1040.73 ppm
P(2): 128.94 ppm
P(3): 128.94 ppm
C(16): 193.11 ppm
H(32): 30.91 ppm
H(33): 31.81 ppm
H(34): 30.91 ppm
```

Coupling Constants

```
C(16)-H(32) k=44.576 j=134.666
C(16)-H(33) k=43.270 j=130.722
C(16)-H(34) k=44.576 j=134.666
C(16)-Rh(1) k=204.065 j=-19.496
C(16)-P(2) k=-4.140 j=-5.069
Rh(1)-P(2) k=910.905 j=-140.220
Rh(1)-H(32) k=-3.399 j=1.291
Rh(1)-H(33) k=-4.921 j=1.869
Rh(1)-H(34) k=-3.399 j=1.291
P(2)-H(32) k=0.482 j=2.346
P(2)-H(33) k=-0.032 j=-0.155
P(2)-H(34) k=2.975 j=14.480
```

$LRhCH_3$ ZSO-KT2/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants

```
Rh(1): -627.84 ppm
P(2): 148.61 ppm
P(3): 148.61 ppm
C(16): 205.78 ppm
H(32): 30.80 ppm
H(33): 31.40 ppm
H(34): 30.80 ppm
```

Coupling Constants

```
C(16)-H(32) k=44.612 j=134.775
C(16)-H(33) k=43.267 j=130.710
C(16)-H(34) k=44.612 j=134.775
C(16)-Rh(1) k=214.982 j=-20.539
C(16)-P(2) k=-4.355 j=-5.332
Rh(1)-P(2) k=923.088 j=-142.095
Rh(1)-H(32) k=-3.889 j=1.477
Rh(1)-H(33) k=-5.608 j=2.130
Rh(1)-H(34) k=-3.889 j=1.477
P(2)-H(32) k=0.465 j=2.266
P(2)-H(33) k=-0.042 j=-0.204
P(2)-H(34) k=2.961 j=14.413
```

L′Rh(H)CH$_3$ ZSO-KT2/TZ2P//Model geom[1]

Shielding Constants
Rh(1): -1115.53 ppm
P(2): 152.39 ppm
C(12): 182.57 ppm
H(32): 29.61 ppm
H(33): 30.61 ppm
H(34): 29.61 ppm
H(35): 50.34 ppm

Coupling Constants
C(12)-H(32) k=48.596 j=146.811
C(12)-H(33) k=44.094 j=133.209
C(12)-H(34) k=48.597 j=146.813
C(12)-H(35) k=-0.844 j=-2.548
C(12)-Rh(1) k=182.418 j=-17.428
C(12)-P(2) k=-2.188 j=-2.678
Rh(1)-P(2) k=527.928 j=-81.266
Rh(1)-H(32) k=1.438 j=-0.546
Rh(1)-H(33) k=-10.746 j=4.082
Rh(1)-H(34) k=1.438 j=-0.546
Rh(1)-H(35) k=193.833 j=-73.629
P(2)-H(32) k=0.518 j=2.521
P(2)-H(33) k=-0.170 j=-0.830
P(2)-H(34) k=3.863 j=18.805
P(2)-H(35) k=-2.405 j=-11.705

TMS ZSO-KT2/QZ4P//ZSC-BLYP/TZ2P

Shielding Constants
C(2): 186.60 ppm
H(6): 31.11 ppm

L′Rh(H)CH$_3$ ZSO-KT2/QZ4P//Model geom[1]

Shielding Constants
Rh(1): -1199.58 ppm
P(2): 121.00 ppm
C(12): 176.81 ppm
H(32): 29.42 ppm
H(33): 30.31 ppm
H(34): 29.45 ppm
H(35): 50.25 ppm

Coupling Constants
C(12)-H(32) k=45.688 j=138.025
C(12)-H(33) k=41.724 j=126.049
C(12)-H(34) k=45.686 j=138.021
C(12)-H(35) k=-0.879 j=-2.655
C(12)-Rh(1) k=177.642 j=-16.971
C(12)-P(2) k=-2.401 j=-2.939
Rh(1)-P(2) k=559.066 j=-86.060
Rh(1)-H(32) k=1.567 j=-0.595
Rh(1)-H(33) k=-11.070 j=4.205
Rh(1)-H(34) k=1.566 j=-0.595
Rh(1)-H(35) k=202.433 j=-76.896
P(2)-H(32) k=0.520 j=2.533
P(2)-H(33) k=-0.151 j=-0.735
P(2)-H(34) k=3.710 j=18.059
P(2)-H(35) k=-2.530 j=-12.315

[1]Model geom means a model system where the *t*-Bu groups of PONOP have been replaced by methyl groups

L′Ir(H)CH$_3$ ZSO-KT2/TZ2P//Model geom[1]

```
Shielding Constants
Ir(1): 1777.37 ppm
P(3): 164.47 ppm
C(12): 192.22 ppm
H(29): 28.73 ppm
H(33): 29.38 ppm
H(34): 28.71 ppm
H(35): 62.96 ppm

Coupling Constants
C(12)-H(29) k=48.149 j=145.461
C(12)-H(33) k=44.034 j=133.029
C(12)-H(34) k=48.149 j=145.461
C(12)-H(35) k=-0.669 j=-2.020
C(12)-Ir(1) k=609.935 j=0.000
C(12)-P(2) k=-0.986 j=-1.207
Ir(1)-P(2) k=1193.718 j=0.000
Ir(1)-H(29) k=9.031 j=0.000
Ir(1)-H(33) k=-39.789 j=0.000
Ir(1)-H(34) k=9.031 j=0.000
Ir(1)-H(35) k=760.445 j=0.000
P(2)-H(29) k=1.197 j=5.825
P(2)-H(33) k=-0.249 j=-1.213
P(2)-H(34) k=2.796 j=13.610
P(2)-H(35) k=-1.903 j=-9.264
```

L′Ir(H)CH$_3$ ZSO-KT2/QZ4P//Model geom[1]

```
Shielding Constants
Ir(1): 1932.07 ppm
P(3): 136.38 ppm
C(12): 187.73 ppm
H(29): 28.86 ppm
H(33): 29.33 ppm
H(34): 28.89 ppm
H(35): 63.71 ppm

Coupling Constants
C(12)-H(29) k=43.987 j=132.887
C(12)-H(33) k=39.132 j=118.220
C(12)-H(34) k=43.988 j=132.889
C(12)-H(35) k=-0.707 j=-2.136
C(12)-Ir(1) k=637.912 j=0.000
C(12)-P(2) k=-1.215 j=-1.488
Ir(1)-P(2) k=1411.038 j=0.000
Ir(1)-H(29) k=11.112 j=0.000
Ir(1)-H(33) k=-44.430 j=0.000
Ir(1)-H(34) k=11.113 j=0.000
Ir(1)-H(35) k=873.477 j=0.000
P(2)-H(29) k=1.244 j=6.055
P(2)-H(33) k=-0.227 j=-1.104
P(2)-H(34) k=2.644 j=12.872
P(2)-H(35) k=-2.111 j=-10.274
```

[1]Model geom means a model system where the *t*-Bu groups of PONOP have been replaced by methyl groups

TMS ZSO-SAOP/TZ2P//ZSC-BLYP/TZ2P

Shielding Constants
C(2): 186.45 ppm
H(6): 31.74 ppm

LIr(H)CH_3^+ ZSO-SAOP/TZ2P//BLYP/TZ2P

Shielding Constants
Ir(1): 2086.38 ppm
P(2): 148.22 ppm
P(3): 148.22 ppm
C(16): 186.10 ppm
H(29): 29.17 ppm
H(33): 29.90 ppm
H(34): 29.17 ppm
H(35): 60.36 ppm

LIrCH_4^+ ZSO-SAOP/TZ2P//BLYP/TZ2P

Shielding Constants
Ir(1): 3413.78 ppm
P(2): 150.71 ppm
P(3): 150.71 ppm
C(16): 226.27 ppm
H(29): 31.58 ppm
H(33): 28.37 ppm
H(34): 31.58 ppm
H(35): 37.32 ppm

LRh(H)CH_3^+ ZSO-SAOP/TZ2P//BLYP/TZ2P

Shielding Constants
Rh(1): -583.03 ppm
P(2): 142.25 ppm
P(3): 142.25 ppm
C(16): 174.89 ppm
H(32): 29.87 ppm
H(33): 30.65 ppm
H(34): 29.87 ppm
H(35): 46.74 ppm

LRhCH_4^+ ZSO-SAOP/TZ2P//BLYP/TZ2P

Shielding Constants
Rh(1): -419.57 ppm
P(2): 133.35 ppm
P(3): 133.35 ppm
C(16): 218.22 ppm
H(32): 32.16 ppm
H(33): 29.38 ppm
H(34): 32.16 ppm
H(35): 35.55 ppm

$LIrCH_4^+$ ZSC-BLYP/TZ2P//M4
$LIrCH_4^+$ ZSC-BLYP/TZ2P//M4

Shielding Constants

```
Ir(1): 725.76 ppm
P(2): 66.36 ppm
P(3): 66.36 ppm
C(16): 201.54 ppm
H(29): 31.63 ppm
H(33): 26.78 ppm
H(34): 31.63 ppm
H(35): 34.00 ppm
```

$LIrCH_4^+$ ZSO-BLYP/TZ2P//M4
$LIrCH_4^+$ ZSO-BLYP/TZ2P//M4

Shielding Constants

```
Ir(1): 3152.29 ppm
P(2): 81.36 ppm
P(3): 81.35 ppm
C(16): 223.90 ppm
H(29): 31.19 ppm
H(33): 27.56 ppm
H(34): 31.19 ppm
H(35): 35.71 ppm
```

$LIrCH_4^+$ ZSC-M06-L/TZ2P//M4

Shielding Constants

```
Ir(1): 1542.93 ppm
P(2): 171.74 ppm
P(3): 171.79 ppm
C(16): 217.84 ppm
H(29): 30.22 ppm
H(33): 32.10 ppm
H(34): 30.23 ppm
H(35): 40.08 ppm
```

$LIrCH_4^+$ ZSO-M06-L/TZ2P//M4

Shielding Constants

```
Ir(1): 3949.26 ppm
P(2): 185.48 ppm
P(3): 185.54 ppm
C(16): 237.87 ppm
H(29): 30.05 ppm
H(33): 32.41 ppm
H(34): 30.06 ppm
H(35): 42.06 ppm
```

$LIr(H)CH_3^+$ BLYP/TZ2P//M4 (**NON REL**)

Shielding Constants

```
Ir(1): 860.83 ppm
P(2): 64.44 ppm
P(3): 64.44 ppm
C(16): 166.12 ppm
H(29): 29.66 ppm
H(33): 31.00 ppm
H(34): 29.66 ppm
H(35): 40.44 ppm
```

$LIr(H)CH_3^+$ BLYP/TZ2P//M4 (**NON REL**)

Coupling Constants

```
C(16)-H(29) k=51.657    j=156.057
C(16)-H(33) k=48.792    j=147.403
C(16)-H(34) k=51.655    j=156.052
C(16)-H(35) k=-0.435    j=-1.314
C(16)-Ir(1) k=451.560   j=0.000
C(16)-P(2) k=-4.099     j=-5.018
Ir(1)-P(2) k=1220.052   j=0.000
Ir(1)-H(29) k=-1.312    j=0.000
Ir(1)-H(33) k=-22.514   j=0.000
Ir(1)-H(34) k=-1.310    j=0.000
Ir(1)-H(35) k=426.154   j=0.000
P(2)-H(29) k=-0.034     j=-0.167
P(2)-H(33) k=-0.250     j=-1.218
P(2)-H(34) k=3.491      j=16.992
P(2)-H(35) k=0.038      j=0.186
```

M4 means geometries optimized in Ref. W. H. Bernskoetter, C. K. Schauer, K. I. Goldberg and M. Brookhart, *Science*, 2009, **326**, 553 at the M4 level.

$LIr(H)CH_3^+$ ZSC-BLYP/TZ2P//M4
$LIr(H)CH_3^+$ ZSC-BLYP/TZ2P//M4

Shielding Constants

Ir(1): -764.90 ppm
P(2): 73.60 ppm
P(3): 73.60 ppm
C(16): 162.14 ppm
H(29): 29.71 ppm
H(33): 30.84 ppm
H(34): 29.71 ppm
H(35): 43.84 ppm

Coupling Constants

C(16)-H(29)	k=51.180	j=154.618
C(16)-H(33)	k=47.575	j=143.726
C(16)-H(34)	k=51.178	j=154.610
C(16)-H(35)	k=-1.326	j=-4.005
C(16)-Ir(1)	k=763.482	j=0.000
C(16)-P(2)	k=-3.054	j=-3.739
Ir(1)-P(2)	k=1478.668	j=0.000
Ir(1)-H(29)	k=0.135	j=0.000
Ir(1)-H(33)	k=-42.548	j=0.000
Ir(1)-H(34)	k=0.136	j=0.000
Ir(1)-H(35)	k=836.423	j=0.000
P(2)-H(29)	k=0.688	j=3.351
P(2)-H(33)	k=-0.222	j=-1.079
P(2)-H(34)	k=2.466	j=12.001
P(2)-H(35)	k=-2.402	j=-11.691

$LIr(H)CH_3^+$ ZSO-BLYP/TZ2P//M4
$LIr(H)CH_3^+$ ZSO-BLYP/TZ2P//M4

Shielding Constants

Ir(1): 1760.05 ppm
P(2): 82.53 ppm
P(3): 82.53 ppm
C(16): 177.07 ppm
H(29): 28.84 ppm
H(33): 29.35 ppm
H(34): 28.84 ppm
H(35): 63.01 ppm

Coupling Constants

C(16)-H(29)	k=51.273	j=154.898
C(16)-H(33)	k=47.477	j=143.429
C(16)-H(34)	k=51.271	j=154.891
C(16)-H(35)	k=-1.228	j=-3.710
C(16)-Ir(1)	k=774.745	j=0.000
C(16)-P(2)	k=-3.493	j=-4.276
Ir(1)-P(2)	k=1430.796	j=0.000
Ir(1)-H(29)	k=-1.772	j=0.000
Ir(1)-H(33)	k=-45.362	j=0.000
Ir(1)-H(34)	k=-1.769	j=0.000
Ir(1)-H(35)	k=891.294	j=0.000
P(2)-H(29)	k=0.669	j=3.256
P(2)-H(33)	k=-0.246	j=-1.199
P(2)-H(34)	k=2.412	j=11.742
P(2)-H(35)	k=-2.198	j=-10.698

$LIr(H)CH_3^+$ ZSC-M06-L/TZ2P//M4
$LIr(H)CH_3^+$ ZSC-M06-L/TZ2P//M4

Shielding Constants

```
Ir(1): 96.92 ppm
P(2): 179.06 ppm
P(3): 179.07 ppm
C(16): 176.99 ppm
H(29): 30.39 ppm
H(33): 31.26 ppm
H(34): 30.39 ppm
H(35): 49.09 ppm
```

$LIr(H)CH_3^+$ ZSO-M06-L/TZ2P//M4

Shielding Constants

```
Ir(1): 2577.13 ppm
P(2): 191.25 ppm
P(3): 191.25 ppm
C(16): 192.59 ppm
H(29): 29.65 ppm
H(33): 30.17 ppm
H(34): 29.65 ppm
H(35): 65.60 ppm
```

$LIr(H)CH_3^+$ ZSC-KT2/TZ2P//M4
Shielding Constants

```
Ir(1): -547.09 ppm
P(2): 159.50 ppm
P(3): 159.51 ppm
C(16): 173.27 ppm
H(29): 29.47 ppm
H(33): 30.65 ppm
H(34): 29.47 ppm
H(35): 43.00 ppm
```

Coupling Constants

```
C(16)-H(29) k=45.460    j=137.335
C(16)-H(33) k=42.039    j=127.000
C(16)-H(34) k=45.457    j=137.329
C(16)-H(35) k=-0.680    j=-2.054
C(16)-Ir(1) k=636.549   j=0.000
C(16)-P(2) k=-1.177     j=-1.441
Ir(1)-P(2) k=1238.256   j=0.000
Ir(1)-H(29) k=9.859     j=0.000
Ir(1)-H(33) k=-33.182   j=0.000
Ir(1)-H(34) k=9.861     j=0.000
Ir(1)-H(35) k=657.489   j=0.000
P(2)-H(29) k=0.771      j=3.754
P(2)-H(33) k=-0.176     j=-0.858
P(2)-H(34) k=2.279      j=11.093
P(2)-H(35) k=-1.517     j=-7.383
```

$LIr(H)CH_3^+$ ZSO-KT2/TZ2P//M4
Shielding Constant

```
Ir(1): 1969.51 ppm
P(2): 168.54 ppm
P(3): 168.54 ppm
C(16): 189.59 ppm
H(29): 28.32 ppm
H(33): 29.24 ppm
H(34): 28.32 ppm
H(35): 61.79 ppm
```

Coupling Constants

```
C(16)-H(29) k=45.540    j=137.580
C(16)-H(33) k=41.942    j=126.708
C(16)-H(34) k=45.538    j=137.573
C(16)-H(35) k=-0.603    j=-1.822
C(16)-Ir(1) k=643.653   j=0.000
C(16)-P(2) k=-1.587     j=-1.943
Ir(1)-P(2) k=1195.198   j=0.000
Ir(1)-H(29) k=8.102     j=0.000
Ir(1)-H(33) k=-35.685   j=0.000
Ir(1)-H(34) k=8.104     j=0.000
Ir(1)-H(35) k=702.890   j=0.000
P(2)-H(29) k=0.753      j=3.667
P(2)-H(33) k=-0.200     j=-0.975
P(2)-H(34) k=2.228      j=10.844
P(2)-H(35) k=-1.394     j=-6.786
```

$LRhCH_4^+$ ZSC-BLYP/TZ2P//M4
$LRhCH_4^+$ ZSC-BLYP/TZ2P//M4
Shielding Constants

```
Rh(1): -1233.55 ppm
P(2): 41.88 ppm
P(3): 41.90 ppm
C(16): 210.14 ppm
H(32): 32.19 ppm
H(33): 28.54 ppm
H(34): 32.19 ppm
H(35): 33.22 ppm
```

Coupling Constants

```
C(16)-H(32) k=57.048    j=172.344
C(16)-H(33) k=41.833    j=126.379
C(16)-H(34) k=57.048    j=172.345
C(16)-H(35) k=31.540    j=95.283
C(16)-Rh(1) k=-62.115   j=5.934
C(16)-P(2) k=-0.714     j=-0.875
Rh(1)-P(2) k=717.704    j=-110.479
Rh(1)-H(32) k=11.944    j=-4.537
Rh(1)-H(33) k=28.395    j=-10.786
Rh(1)-H(34) k=11.947    j=-4.538
Rh(1)-H(35) k=55.756    j=-21.179
P(2)-H(32) k=0.484      j=2.356
P(2)-H(33) k=-0.248     j=-1.206
P(2)-H(34) k=1.179      j=5.740
P(2)-H(35) k=-0.469     j=-2.283
```

$LRhCH_4^+$ ZSO-BLYP/TZ2P//M4
Shielding Constants

```
Rh(1): -783.10 ppm
P(2): 65.33 ppm
P(3): 65.34 ppm
C(16): 219.60 ppm
H(32): 32.18 ppm
H(33): 29.18 ppm
H(34): 32.18 ppm
H(35): 34.31 ppm
```

Coupling Constants

```
C(16)-H(32) k=57.057    j=172.371
C(16)-H(33) k=41.872    j=126.496
C(16)-H(34) k=57.057    j=172.373
C(16)-H(35) k=31.562    j=95.351
C(16)-Rh(1) k=-57.585   j=5.501
C(16)-P(2) k=-0.824     j=-1.009
Rh(1)-P(2) k=729.343    j=-112.271
Rh(1)-H(32) k=11.680    j=-4.437
Rh(1)-H(33) k=28.433    j=-10.801
Rh(1)-H(34) k=11.683    j=-4.438
Rh(1)-H(35) k=55.734    j=-21.171
P(2)-H(32) k=0.481      j=2.343
P(2)-H(33) k=-0.253     j=-1.231
P(2)-H(34) k=1.167      j=5.678
P(2)-H(35) k=-0.484     j=-2.357
```

$LRhCH_4^+$ BLYP/TZ2P//M4 (**NON REL**)
Shielding Constants

```
Rh(1): -994.91 ppm
P(2): 37.26 ppm
P(3): 37.26 ppm
C(16): 209.86 ppm
H(32): 32.08 ppm
H(33): 28.62 ppm
H(34): 32.08 ppm
H(35): 32.94 ppm
```

$LRhCH_4^+$ BLYP/TZ2P//M4 (**NON REL**)
Coupling Constants

```
C(16)-H(32) k=56.990    j=172.169
C(16)-H(33) k=42.272    j=127.706
C(16)-H(34) k=56.990    j=172.168
C(16)-H(35) k=32.241    j=97.400
C(16)-Rh(1) k=-24.713   j=2.361
C(16)-P(2) k=-1.269     j=-1.554
Rh(1)-P(2) k=594.753    j=-91.553
Rh(1)-H(32) k=10.398    j=-3.950
Rh(1)-H(33) k=24.075    j=-9.145
Rh(1)-H(34) k=10.401    j=-3.951
Rh(1)-H(35) k=46.077    j=-17.503
P(2)-H(32) k=0.310      j=1.511
P(2)-H(33) k=-0.239     j=-1.162
P(2)-H(34) k=1.432      j=6.969
P(2)-H(35) k=-0.411     j=-2.000
```

$LRhCH_4^+$ ZSC-M06-L/TZ2P//M4
$LRhCH_4^+$ ZSC-M06-L/TZ2P//M4
Shielding Constants

```
Rh(1): -568.12 ppm
P(2): 141.99 ppm
P(3): 141.96 ppm
C(16): 222.90 ppm
H(32): 30.32 ppm
H(33): 34.75 ppm
H(34): 30.32 ppm
H(35): 38.75 ppm
```

Coupling Constants

```
C(16)-H(32) k=48.716    j=147.171
C(16)-H(33) k=34.045    j=102.850
C(16)-H(34) k=48.728    j=147.208
C(16)-H(35) k=24.444    j=73.845
C(16)-Rh(1) k=-31.517   j=3.011
C(16)-P(2) k=0.062      j=0.076
Rh(1)-P(2) k=544.708    j=-83.849
Rh(1)-H(32) k=9.534     j=-3.622
Rh(1)-H(33) k=20.087    j=-7.630
Rh(1)-H(34) k=9.540     j=-3.624
Rh(1)-H(35) k=39.940    j=-15.172
P(2)-H(32) k=0.456      j=2.217
P(2)-H(33) k=-0.114     j=-0.554
P(2)-H(34) k=0.818      j=3.979
P(2)-H(35) k=-0.207     j=-1.007
```

$LRhCH_4^+$ ZSO-M06-L/TZ2P//M4
$LRhCH_4^+$ ZSO-M06-L/TZ2P//M4
Shielding Constants

```
Rh(1): -130.74 ppm
P(2): 162.17 ppm
P(3): 162.14 ppm
C(16): 230.82 ppm
H(32): 30.36 ppm
H(33): 35.17 ppm
H(34): 30.36 ppm
H(35): 39.61 ppm
```

$LRhCH_4^+$ ZSC-BLYP/QZ4P//M4
Shielding Constants

```
Rh(1): -1310.37 ppm
P(2): 21.31 ppm
P(3): 21.33 ppm
C(16): 206.61 ppm
H(32): 31.98 ppm
H(33): 28.27 ppm
H(34): 31.98 ppm
H(35): 33.05 ppm
```

$LRhCH_4^+$ ZSC-KT2/TZ2P//M4
$LRhCH_4^+$ ZSC-KT2/TZ2P//M4
Shielding Constants

```
Rh(1): -1083.84 ppm
P(2): 125.34 ppm
P(3): 125.35 ppm
C(16): 219.57 ppm
H(32): 32.04 ppm
H(33): 28.30 ppm
H(34): 32.04 ppm
H(35): 33.04 ppm
```

Coupling Constants

```
C(16)-H(32) k=51.475    j=155.509
C(16)-H(33) k=35.811    j=108.187
C(16)-H(34) k=51.476    j=155.512
C(16)-H(35) k=25.938    j=78.360
C(16)-Rh(1) k=-44.964   j=4.296
C(16)-P(2) k=-0.050     j=-0.062
Rh(1)-P(2) k=600.358    j=-92.416
Rh(1)-H(32) k=12.358    j=-4.694
Rh(1)-H(33) k=24.690    j=-9.379
Rh(1)-H(34) k=12.362    j=-4.696
Rh(1)-H(35) k=51.175    j=-19.439
P(2)-H(32) k=0.573      j=2.791
P(2)-H(33) k=-0.142     j=-0.691
P(2)-H(34) k=1.122      j=5.461
P(2)-H(35) k=-0.266     j=-1.295
```

$LRhCH_4^+$ ZSO-KT2/TZ2P//M
$LRhCH_4^+$ ZSO-KT2/TZ2P//M
Shielding Constants

```
Rh(1): -632.58 ppm
P(2): 146.72 ppm
P(3): 146.72 ppm
C(16): 229.33 ppm
H(32): 32.02 ppm
H(33): 28.79 ppm
H(34): 32.02 ppm
H(35): 34.07 ppm
```

Coupling Constants

```
C(16)-H(32) k=51.482    j=155.530
C(16)-H(33) k=35.849    j=108.303
C(16)-H(34) k=51.483    j=155.533
C(16)-H(35) k=25.960    j=78.427
C(16)-Rh(1) k=-40.699   j=3.888
C(16)-P(2) k=-0.150     j=-0.184
Rh(1)-P(2) k=610.036    j=-93.906
Rh(1)-H(32) k=12.129    j=-4.607
Rh(1)-H(33) k=24.716    j=-9.389
Rh(1)-H(34) k=12.133    j=-4.609
Rh(1)-H(35) k=51.186    j=-19.443
P(2)-H(32) k=0.570      j=2.774
P(2)-H(33) k=-0.148     j=-0.721
P(2)-H(34) k=1.110      j=5.405
P(2)-H(35) k=-0.282     j=-1.374
```

LRh(H)CH_3^+ ZSC-BLYP/TZ2P//M4
LRh(H)CH_3^+ ZSC-BLYP/TZ2P//M4
Shielding Constants

```
Rh(1): -1407.82 ppm
P(2): 58.94 ppm
P(3): 58.91 ppm
C(16): 163.09 ppm
H(32): 29.93 ppm
H(33): 30.87 ppm
H(34): 29.93 ppm
H(35): 42.19 ppm
```

LRh(H)CH_3^+ ZSO-BLYP/TZ2P//M4
LRh(H)CH_3^+ ZSO-BLYP/TZ2P//M4
Shielding Constants

```
Rh(1): -994.02 ppm
P(2): 77.59 ppm
P(3): 77.56 ppm
C(16): 172.20 ppm
H(32): 29.90 ppm
H(33): 30.90 ppm
H(34): 29.90 ppm
H(35): 50.17 ppm
```

LRh(H)CH_3^+ ZSC-M06-L/TZ2P//M4
Shielding Constants

```
Rh(1): -730.72 ppm
P(2): 160.78 ppm
P(3): 160.73 ppm
C(16): 175.02 ppm
H(32): 30.64 ppm
H(33): 31.84 ppm
H(34): 30.64 ppm
H(35): 45.56 ppm
```

LRh(H)CH_3^+ ZSO-M06-L/TZ2P//M4
Shielding Constants

```
Rh(1): -321.06 ppm
P(2): 178.17 ppm
P(3): 178.12 ppm
C(16): 184.24 ppm
H(32): 30.59 ppm
H(33): 31.85 ppm
H(34): 30.59 ppm
H(35): 52.34 ppm
```

LRh(H)CH_3^+ ZSC-KT2/TZ2P//M4

LRh(H)CH_3^+ ZSC-KT2/TZ2P//M4

Shielding Constants

```
Rh(1): -1186.68 ppm
P(2): 143.68 ppm
P(3): 143.66 ppm
C(16): 174.35 ppm
H(32): 29.64 ppm
H(33): 30.67 ppm
H(34): 29.64 ppm
H(35): 41.17 ppm
```

Coupling Constants

```
C(16)-H(32) k=46.396    j=140.164
C(16)-H(33) k=43.097    j=130.198
C(16)-H(34) k=46.397    j=140.168
C(16)-H(35) k=-0.836    j=-2.527
C(16)-Rh(1) k=184.591   j=-17.635
C(16)-P(2) k=-2.333     j=-2.856
Rh(1)-P(2) k=508.105    j=-78.215
Rh(1)-H(32) k=2.083     j=-0.791
Rh(1)-H(33) k=-10.447   j=3.968
Rh(1)-H(34) k=2.082     j=-0.791
Rh(1)-H(35) k=164.902   j=-62.639
P(2)-H(32) k=0.375      j=1.824
P(2)-H(33) k=-0.148     j=-0.722
P(2)-H(34) k=3.217      j=15.661
P(2)-H(35) k=-1.307     j=-6.360
```

LRh(H)CH_3^+ ZSO-KT2/TZ2P//M4

Shielding Constants

```
Rh(1): -773.32 ppm
P(2): 160.95 ppm
P(3): 160.93 ppm
C(16): 183.94 ppm
H(32): 29.51 ppm
H(33): 30.65 ppm
H(34): 29.51 ppm
H(35): 49.02 ppm
```

Coupling Constants

```
C(16)-H(32) k=46.439    j=140.293
C(16)-H(33) k=43.090    j=130.177
C(16)-H(34) k=46.440    j=140.297
C(16)-H(35) k=-0.842    j=-2.543
C(16)-Rh(1) k=191.718   j=-18.316
C(16)-P(2) k=-2.468     j=-3.021
Rh(1)-P(2) k=512.876    j=-78.949
Rh(1)-H(32) k=1.647     j=-0.626
Rh(1)-H(33) k=-10.730   j=4.076
Rh(1)-H(34) k=1.646     j=-0.625
Rh(1)-H(35) k=176.435   j=-67.020
P(2)-H(32) k=0.366      j=1.783
P(2)-H(33) k=-0.150     j=-0.729
P(2)-H(34) k=3.212      j=15.633
P(2)-H(35) k=-1.268     j=-6.170
```

[1]For Si, Rh and Ir we used the LANL08d and LANL08(f) of Refs. P.J. Hay and W.R. Wadt, J. Chem. Phys. 82, 299 (1985); L.E. Roy, P.J. Hay, and R.L. Martin, J. Chem. Theory Comput. 4, 1029 (2008); A.W. Ehlers, M. Bohme, S. Dapprich, A. Gobbi, A. Hollwarth, V. Jonas, K.F. Kohler, R. Stegmann, A. Veldkamp, G. Frenking, Chem. Phys. Lett. 208, 111 (1993); C.E. Check, T.O. Faust, J.M. Bailey, B.J. Wright, T.M. Gilbert and L.S. Sunderlin, J Phys. Chem. A 105, 8111 (2001)

CH4 ZSC-KT2/TZ2P//BLYP/TZ2P
Shielding Constants
C(1): 198.22 ppm
H(2): 31.27 ppm

Coupling Constants
C(1)-H(2) k=44.932 j=135.740

CH4 ZSO-KT2/TZ2P//BLYP/TZ2P
Shielding Constants
C(1): 199.01 ppm
H(2): 31.28 ppm

Coupling Constants
C(1)-H(2) k=44.919 j=135.703

TMS ZSC-KT2/TZ2P//BLYP/TZ2P
Shielding Constants
C(2): 190.53 ppm
H(6): 31.33 ppm

TMS ZSO-KT2/TZ2P//BLYP/TZ2P
Shielding Constants
C(2): 191.44 ppm
H(6): 31.34 ppm

TMS MP2/cc-pVTZ[1]// BLYP/TZ2P
Shielding Constants
C(2): 199.18 ppm
H(6): 31.53 ppm

TMS ZSO-SAOP/TZ2P//BLYP/TZ2P
Shielding Constants
C(2): 186.45 ppm
H(6): 31.74 ppm

TMS HF/cc-pVTZ[1]// BLYP/TZ2P
Shielding Constants
C(2): 194.91 ppm
H(6): 31.91 ppm

$CH5^+$ ZSC-KT2/TZ2P//BLYP/TZ2P
Shielding Constants
C(1): 212.23 ppm
H(2): 28.85 ppm
H(3): 26.22 ppm
H(4): 28.85 ppm
H(5): 26.79 ppm
H(6): 26.40 ppm

Coupling Constants
C(1)-H(2) k=61.620 j=186.56
C(1)-H(3) k=42.827 j=129.382
C(1)-H(4) k=61.579 j=186.034
C(1)-H(5) k=13.796 j=41.678
C(1)-H(6) k=19.315 j=58.351

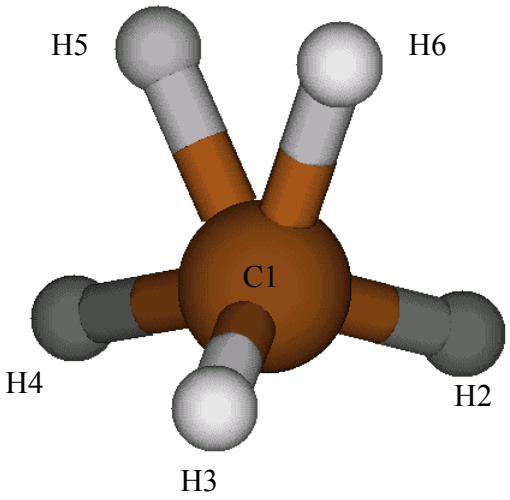


Figure S1. CH_5^+ optimized structure