Supporting Information

Competing Reaction Pathways of 3,3,3-Trifluoropropene at Rhodium Hydrido, Silyl and Germyl Complexes: C–F Bond Activation versus Hydrogermylation

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The calculations were run using the Gaussian 09 (Revision D.01) program package[1] and the B3LYP functional. Plausible ligand arrangements for [Rh{Si(OEt)$_3$}(CH$_2$CHCF$_3$)(PEt$_3$)$_2$] (**2**) and *fac*-[Rh(H)(CH$_2$CHCF$_3$)(PEt$_3$)$_3$] (**5**) were optimized and the depicted structures turned out to be the minima. The cc-pVTZ basis sets were employed for all rhodium- and silicon-bound atoms (cc-pVDZ for all other carbon and hydrogen atoms). Rhodium was described on using RECPs with the associated cc-pVTZ-PP basis set.[2] Frequency calculations were run for all stationary points to identify them as minima (no negative eigenvalues). Energies were corrected for zero-point energy.

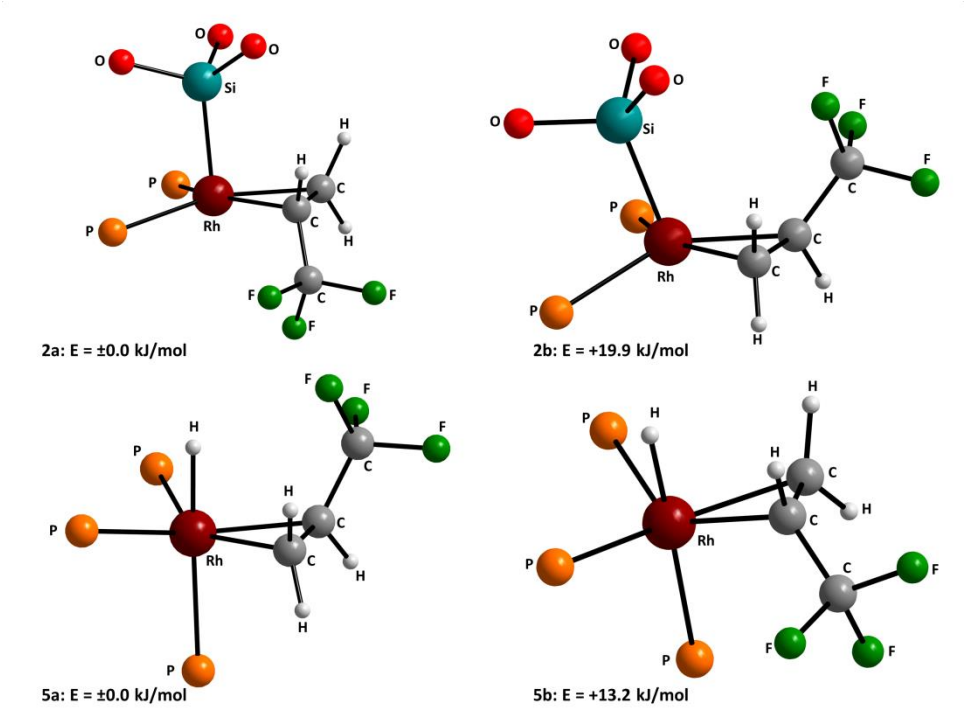

Figure 1. DFT-optimized structures of [Rh(CH$_2$CHCF$_3$){Si(OEt)$_3$}(PEt$_3$)$_2$] (**2**) and *fac*-[Rh(H)(CH$_2$CHCF$_3$)(PEt$_3$)$_3$] (**5**) as well as their energies. The ethyl groups of the phosphine ligands as well as of the silyl ligand have been omitted for clarity.

Optimized cartesian coordinates for complex [Rh(CH$_2$CHCF$_3$){Si(OEt)$_3$}(PEt$_3$)$_2$] (**2a**), energies are corrected for zero-point energy and given in Hartree:
Energy: -2436.707295

Rh	-0.15336	0.28359	-0.68161
Si	1.10574	-1.29036	0.32859
O	0.74254	-1.37374	1.96924
O	2.74717	-1.01630	0.18935
O	0.95665	-2.84342	-0.27271
P	-1.86629	0.51098	1.00029
P	1.44120	1.92676	-0.11114
C	-0.07347	-3.78587	0.00423
C	1.54742	-2.11673	2.88969
C	3.78269	-2.00253	0.12903
C	0.20652	-5.07533	-0.75249
C	0.89549	-2.11109	4.26359
C	4.31061	-2.17084	-1.28902
C	-2.78490	-1.08755	1.27005
C	-3.75837	-1.27701	2.44061

C	-1.46844	1.12617	2.71559
C	-2.55165	1.77431	3.58743
C	-3.10435	1.74802	0.33836
C	-4.59185	1.63720	0.69977
C	3.01768	2.01148	-1.09009
C	2.02485	2.06873	1.66524
C	2.83423	2.22425	-2.59610
C	3.44910	2.55223	1.96210
C	0.65931	3.58942	-0.43268
C	1.49648	4.85232	-0.19667
H	-1.05624	-3.37841	-0.29512
H	-0.12489	-3.98382	1.09143
H	0.23672	-4.88995	-1.83779
H	-0.58042	-5.81982	-0.54815
H	1.17628	-5.50263	-0.45122
H	1.67235	-3.15758	2.53561
H	2.55726	-1.67009	2.94567
H	-0.10845	-2.56340	4.22402
H	0.79431	-1.08275	4.64614
H	1.50504	-2.68586	4.98015
H	3.41692	-2.97162	0.50725
H	4.59377	-1.66462	0.79903
H	3.51666	-2.53612	-1.95872
H	5.13870	-2.89969	-1.30351
H	4.68847	-1.21501	-1.68656
H	-1.97882	-1.83172	1.35578
H	-3.28133	-1.29381	0.30846
H	-3.25562	-1.15960	3.41310
H	-4.17376	-2.29863	2.41458
H	-4.60678	-0.57907	2.41020
H	-0.64731	1.84436	2.57376
H	-1.00979	0.26301	3.22360
H	-2.96742	2.67996	3.11820
H	-2.12105	2.08196	4.55550
H	-3.38812	1.09514	3.80146
H	-3.00438	1.70163	-0.75655
H	-2.70991	2.73684	0.63230
H	-5.01432	0.67770	0.36457
H	-5.16014	2.43502	0.19306
H	-4.77697	1.73358	1.77941
H	3.51598	1.04967	-0.90006
H	3.66018	2.80336	-0.67509
H	2.21553	1.43362	-3.04241
H	3.81286	2.21290	-3.10310
H	2.36137	3.19320	-2.82564
H	1.29327	2.72981	2.16036
H	1.87434	1.07184	2.10335
H	3.64536	3.56341	1.57337
H	4.20351	1.87414	1.53563
H	3.61465	2.58215	3.05212
H	0.29717	3.56008	-1.47398
H	-0.24704	3.61300	0.19483
H	2.40010	4.87359	-0.82570
H	1.81745	4.94041	0.85310
H	0.90903	5.75404	-0.43617
C	0.31278	-0.48101	-2.59552
C	-0.97141	-0.98996	-2.18296
C	-2.19197	-0.47978	-2.85076
H	-1.06813	-2.04330	-1.95884
H	1.13596	-1.17766	-2.68364
H	0.33307	0.29605	-3.35325
F	-2.18320	0.88134	-2.99640
F	-3.33522	-0.77790	-2.17261
F	-2.38421	-0.97330	-4.10422

Optimized cartesian coordinates for complex $[Rh(CH_2CHCF_3)\{Si(OEt)_3\}(PEt_3)_2]$ (**2b**), energies are corrected for zero-point energy and given in Hartree:
Energy: -2436.699711

Rh	-0.05004	0.24180	-0.88312
Si	0.41784	-1.14262	0.84576
O	-0.86855	-1.19813	1.92564
O	1.70832	-0.63786	1.76654
O	0.82242	-2.71554	0.48596
P	-2.37743	0.03864	-0.61881
P	0.54230	2.17870	0.40663
C	0.01508	-3.78321	0.01574
C	-0.75220	-1.87271	3.18479
C	3.04161	-1.15924	1.78582
C	0.85450	-5.04961	-0.06662
C	-2.07800	-1.80172	3.92593
C	3.68156	-0.84619	3.12950
C	-3.05255	-1.69220	-0.74982
C	-4.52154	-2.01421	-0.44764
C	-3.28440	0.81546	0.81316
C	-4.74718	1.25850	0.67688
C	-3.00996	0.96363	-2.12094
C	-4.34443	0.57925	-2.77476
C	2.31998	2.72711	0.39065
C	0.06619	2.25088	2.21820
C	2.82959	3.21145	-0.97182
C	0.91714	3.07065	3.19552
C	-0.34718	3.65917	-0.30784
C	-0.12398	5.04060	0.32012
H	-0.39900	-3.54028	-0.97939
H	-0.84354	-3.93962	0.69744
H	1.70240	-4.90510	-0.75399
H	0.24490	-5.89210	-0.43305
H	1.25723	-5.31640	0.92356
H	-0.46088	-2.92703	3.02357
H	0.04899	-1.40331	3.78245
H	-2.88273	-2.27845	3.34288
H	-2.36570	-0.75533	4.11753
H	-2.00362	-2.32027	4.89600
H	3.62483	-0.70316	0.96813
H	3.01883	-2.24627	1.60682
H	3.70920	0.24094	3.31003
H	4.71675	-1.22506	3.15572
H	3.12046	-1.31469	3.95434
H	-2.41717	-2.27089	-0.06473
H	-2.77777	-2.02619	-1.76458
H	-4.78074	-1.77995	0.59629
H	-4.70063	-3.09346	-0.58851
H	-5.22434	-1.47777	-1.10046
H	-2.67301	1.69045	1.08297
H	-3.15434	0.10764	1.64638
H	-4.87334	2.02241	-0.10655
H	-5.09070	1.70960	1.62315
H	-5.42649	0.42653	0.44622
H	-2.20957	0.87019	-2.87373
H	-3.01920	2.02828	-1.83010
H	-4.34059	-0.46706	-3.11688
H	-4.52384	1.21006	-3.66130
H	-5.20033	0.71037	-2.09731
H	2.90199	1.85434	0.72328
H	2.46747	3.51772	1.14189
H	2.66688	2.46248	-1.75840
H	3.91327	3.40412	-0.92432
H	2.34373	4.15040	-1.28229

H	-0.97657	2.61180	2.22767
H	0.02718	1.20864	2.56064
H	1.00265	4.13016	2.90950
H	1.93540	2.66205	3.28332
H	0.46632	3.03685	4.20154
H	-0.08528	3.68174	-1.37900
H	-1.41915	3.40266	-0.27203
H	0.93688	5.33528	0.30945
H	-0.47012	5.07489	1.36453
H	-0.68387	5.81127	-0.23548
C	1.44559	-0.16123	-2.35743
C	0.31967	-1.04564	-2.52252
C	2.81901	-0.69717	-2.16846
H	0.46472	-2.09871	-2.32439
H	-0.35874	-0.86172	-3.35144
H	1.49903	0.69930	-3.02067
F	3.45850	-0.88316	-3.36360
F	2.86554	-1.88858	-1.53849
F	3.63511	0.14166	-1.46792

Optimized cartesian coordinates for complex *fac*-[Rh(H)(CH_2=$CHCF_3$)(PEt_3)$_3$] (**5a**) energies are corrected for zero-point energy and given in Hartree:
Energy -2263.279185

Rh	0.02141	0.11017	-0.48062
P	-2.03193	-1.09312	-0.47348
P	1.53403	-1.01562	0.99168
P	-0.48057	2.11380	0.85867
C	-0.41168	2.05505	2.72634
C	0.63591	3.60641	0.64434
C	-1.42190	1.14198	3.42469
C	0.47144	4.44113	-0.63285
C	-2.16822	2.85026	0.55824
C	-2.58247	4.10114	1.34241
C	0.89538	-1.73471	2.60305
C	1.60992	-2.89439	3.31071
C	2.31979	-2.46883	0.11926
C	3.69934	-2.99934	0.52782
C	2.96829	0.06922	1.50478
C	3.85263	-0.27820	2.70976
C	-3.43489	-0.71823	0.71508
C	-4.49032	-1.77635	1.06560
C	-1.74596	-2.93139	-0.26233
C	-2.67308	-3.97098	-0.90521
C	-2.83401	-0.91002	-2.15119
C	-4.29595	-1.30370	-2.40082
H	-1.25976	1.14981	4.51518
H	-1.33644	0.10034	3.08370
H	-2.45845	1.47083	3.24777
H	-0.51935	3.08450	3.10658
H	0.61610	1.74652	2.97998
H	1.66607	3.21869	0.70843
H	0.49786	4.25810	1.52311
H	0.64172	3.85636	-1.54674
H	1.19576	5.27224	-0.63401
H	-0.53276	4.88664	-0.70578
H	-2.21456	3.03860	-0.52686
H	-2.88476	2.03556	0.74140
H	-1.89080	4.94297	1.18368
H	-2.63037	3.91259	2.42652
H	-3.58393	4.43855	1.02777
H	-0.13796	-2.04068	2.37276
H	0.79682	-0.87573	3.28855
H	2.35334	-2.15879	-0.93388
H	1.56550	-3.27392	0.16595
H	4.47554	-2.22637	0.41890
H	3.98589	-3.83437	-0.13356
H	3.73329	-3.37342	1.56089
H	1.66348	-3.78951	2.67183
H	1.05520	-3.18015	4.22086
H	2.63389	-2.63885	3.61748
H	2.52231	1.06413	1.66179
H	3.57529	0.17201	0.59115
H	3.27389	-0.32437	3.64611
H	4.62338	0.49941	2.84604
H	4.37546	-1.23764	2.59030
H	-3.92764	0.18135	0.30743
H	-2.94248	-0.39050	1.64178
H	-5.07226	-2.10283	0.19227
H	-5.20330	-1.36787	1.80207
H	-4.03557	-2.67021	1.52035
H	-0.72457	-3.08269	-0.64028
H	-1.68730	-3.09484	0.82825
H	-2.69046	-3.87226	-2.00156
H	-3.70863	-3.90610	-0.54344
H	-2.30843	-4.98743	-0.67955
H	-2.16026	-1.43697	-2.84779
H	-2.70328	0.15767	-2.38583
H	-4.49029	-2.37311	-2.23855
H	-4.56934	-1.07625	-3.44512
H	-4.98790	-0.73501	-1.75947
H	0.30628	-1.10949	-1.41721
C	1.30002	1.17379	-1.83648
C	-0.05595	1.21437	-2.31156
C	2.34712	0.47889	-2.63441
H	1.73745	2.07890	-1.43373
H	-0.30846	0.61759	-3.17823
H	-0.58919	2.15659	-2.28168
F	2.88850	1.30437	-3.58163
F	1.92790	-0.61532	-3.30554
F	3.41305	0.07864	-1.87776

Optimized cartesian coordinates for complex *fac*-[Rh(H)(CH_2=$CHCF_3$)(PEt_3)$_3$] (**5b**) energies are corrected for zero-point energy and given in Hartree:
Energy -2263.268359

Rh	0.03375	-0.06438	-0.57740
P	2.40944	0.28892	-0.56657
P	-1.08574	1.74918	0.52070
P	-0.24723	-1.79799	1.16261
C	-0.18346	-1.18591	2.92934
C	-1.79037	-2.85126	1.33793
C	1.10418	-0.48122	3.36132
C	-1.91355	-4.06220	0.40365
C	1.07440	-3.11516	1.14651
C	1.12955	-4.11277	2.30990
C	-0.21494	2.68785	1.89273
C	-0.54554	4.15297	2.20914
C	-1.51315	3.05915	-0.74373
C	-2.67328	4.03671	-0.52114
C	-2.73808	1.27735	1.26308
C	-3.40000	2.14934	2.33773
C	3.64086	-0.58993	0.54698
C	5.01974	0.01708	0.84098
C	2.82864	2.10037	-0.32735
C	4.01599	2.75145	-1.04858
C	3.03688	-0.13062	-2.27749
C	4.53022	-0.29400	-2.58812

H	0.99251	-0.04745	4.36884
H	1.36841	0.33168	2.66920
H	1.95420	-1.18122	3.40334
H	-0.38975	-2.03354	3.60311
H	-1.04035	-0.50025	3.03410
H	-2.64189	-2.17404	1.17979
H	-1.84716	-3.19339	2.38519
H	-1.80951	-3.78641	-0.65390
H	-2.90633	-4.52675	0.51981
H	-1.16372	-4.83563	0.63049
H	0.94117	-3.64357	0.18835
H	2.03432	-2.59099	1.05665
H	0.18022	-4.65284	2.44693
H	1.36915	-3.61898	3.26480
H	1.91211	-4.86882	2.13107
H	0.85122	2.61124	1.63489
H	-0.33857	2.06752	2.79630
H	-1.69839	2.48487	-1.66292
H	-0.57070	3.60525	-0.92479
H	-3.63093	3.50581	-0.40737
H	-2.77627	4.69838	-1.39768
H	-2.53439	4.67872	0.35990
H	-0.37896	4.80448	1.33711
H	0.11024	4.52063	3.01692
H	-1.58405	4.29403	2.54054
H	-2.59692	0.26194	1.66360
H	-3.40870	1.14736	0.39927
H	-2.76945	2.24572	3.23599
H	-4.35095	1.69167	2.65880
H	-3.62977	3.16276	1.97968
H	3.75748	-1.59652	0.11007
H	3.11382	-0.73912	1.49977
H	5.62981	0.14469	-0.06380
H	5.58142	-0.63966	1.52707
H	4.93725	0.99898	1.33266
H	1.90760	2.63040	-0.60949
H	2.92987	2.23653	0.76327
H	3.91648	2.67569	-2.14243
H	4.98199	2.31079	-0.76538
H	4.05978	3.82597	-0.80227
H	2.57774	0.62128	-2.94095
H	2.52007	-1.07247	-2.51690
H	5.11068	0.62561	-2.42877
H	4.65822	-0.58219	-3.64534
H	4.98969	-1.09203	-1.98391
H	0.34870	1.03762	-1.65095
C	-1.34519	-0.53796	-2.17930
C	-0.26664	-1.47602	-2.18581
C	-2.77707	-0.91258	-2.07865
H	0.46300	-1.40394	-2.98252
H	-0.46044	-2.49668	-1.88135
H	-1.28414	0.25555	-2.91497
F	-3.25157	-1.44783	-3.24381
F	-3.57007	0.17409	-1.84691
F	-3.08577	-1.81505	-1.12093

Optimized cartesian coordinates for CF3CH=CH2 energies are corrected for zero-point energy and given in Hartree:
Energy: -415.742799

C	-2.11260	0.04976	0.00000
C	-0.98645	-0.64262	0.00000
H	-3.07081	-0.45022	0.00000
H	-2.11395	1.13062	-0.00000
H	-0.96968	-1.72455	0.00000
C	0.37189	-0.01792	0.00000
F	0.33725	1.32631	-0.00000
F	1.08234	-0.40156	-1.08368
F	1.08234	-0.40155	1.08368

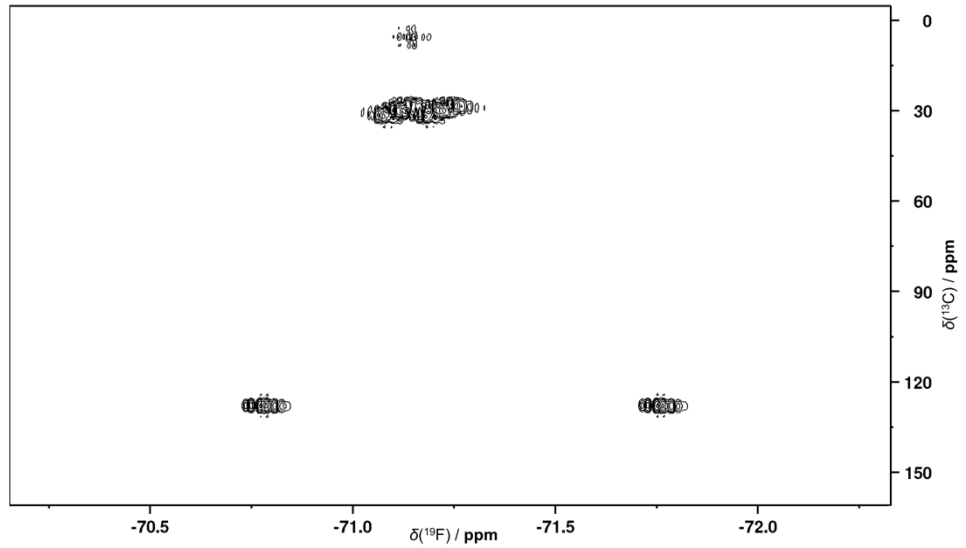

Figure 2. ^{19}F, ^{13}C HMBC NMR spectrum (282.4 MHz/75.4 MHz, [D_6]benzene, optimized on long-range coupling,) of 1,1,1-trifluoropropane-3-triphenylgermane **8**.

1. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F.

Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

2. K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *J. Chem. Phys.*, 2007, **126**, 124101.