Decamethylscandocinium-hydrido-(perfluorophenyl)borate: fixation and tandem tris(perfluorophenyl)borane catalyzed deoxygenative hydrosilation of carbon dioxide

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Supporting Information

General Experimental Methods. An argon filled MBraun glove box was employed for manipulation and storage of all oxygen and moisture sensitive compounds. All reactions were performed on a double manifold high vacuum line using standard techniques. Residual oxygen and moisture were removed from the argon stream by passage through an OxisorBW scrubber from Matheson Gas Products. Hexanes were dried and purified using the Grubbs/Dow purification system, and stored in an evacuated 500mL pressure resistant glass vessel over sodium-tetraglyme/benzophenone ketyl. Benzene was dried over and distilled from and activated 4Å molecular sieves, and stored in a evacuated 500mL pressure resistant glass vessel over sodium-benzophenone ketyl. All solvents were distilled prior to use. D_6-benzene and d_5-bromobenzene were dried over and distilled from activated 4Å molecular sieves and stored in glass bombs in the glove box over activated 4Å molecular sieves. ^{1}H and ^{13}C chemical shifts were referenced to residual proton, and naturally abundant ^{13}C resonances of the deuterated solvents. Assignments of chemical shifts are based on ^{1}H, $^{1}H\{^{11}B\}$, ^{13}C, $^{13}C\{^{1}H\}$, ^{19}F, ^{11}B, $^{1}H,^{13}C$-HSQC, $^{1}H,^{13}C$-HMBC spectroscopy, ROESY, and $^{1}H,^{19}F$-HOESY NMR data performed on Bruker spectrometers equipped with bbo and bbfo probes. ^{11}B NMR spectra were referenced to an external standard of boron trifluoride diethyl etherate (0.0 ppm, d_6-dmso). ^{19}F NMR spectra are referenced to $CFCl_3$ using an external standard of hexafluorobenzene (-163.0 ppm) in C_6D_6. NMR spectra were processed and analyzed with MestReNova (v7.1.0-9185). X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Measurements were collected on a Nonius KappaCCD diffractometer; full details can be found in the independently deposited crystallography information file (cif). IR spectra (FT-IR Nicolet Nexus 470) were taken under a constant flow of N_2 from KBr pellets of the compounds prepared in a glove box. *Tris*-(pentafluorophenyl)borane was doubly sublimed at 65°C in an oil bath under high static vacuum. Triethylsilane was purchased from TCI America and dried over, distilled from, and finally stored over activated 4Å molecular sieves. All compounds were stored in a glove box. Bone Dry Carbon Dioxide, grade 3.0, Praxair, and ^{13}C labeled Carbon Dioxide, 13C 99%, <1% 18O, Cambridge Isotopes, were used as received. Cp^*_2ScCl, and Cp^*_2ScMe were prepared following a reported procedure and stored in a glove box.

Preparation of diisopropoxymethane. A mixture of 5.00g (55.5 mmol) of trioxane, 1.36g (7.1 mmol) 4-toluenesulfonic acid monohydrate, and 8.35g (69.5) anhydrous $MgSO_4$ in 100 mL 2-propanol was refluxed at 84°C until GC-MS monitoring showed complete conversion of the trioxane starting material (~48h). After cooling to r.t., the suspension was filtered through celite. The solution was diluted with a semi concentrated aqueous $NaHCO_3$ solution (total ~400mL), and the product extracted into diethyl ether (3 times, 20 mL), the combined ether fractions dried over $MgSO_4$, and the ether removed under vacuum. The residual liquid was subject to fractional distillation under a slight vacuum, and a colorless liquid collected at a still head temperature of 106°C. The product was dried over 3Å activated molecular sieves overnight, vacuum transferred, degassed by three freeze-pump-thaw cycles and stored over fresh 3Å activated molecular sieves in a glove box. Yield: 1.95g (14.8 mmol), 9%.

Note: The product forms an azeotropic mixture with 2-propanol that distills at almost the same boiling point as the pure alcohol; the product cannot be isolated by distillation.

^{1}H NMR (400 MHz, C_6D_6, 298K): δ 4.66 (s, 2H, (^{i}PrO)$_2$C*H*$_2$); 3.81 (heptet, $^3J_{H\text{-}H}$ = 6.15 Hz, 2H, ^{i}Pr-C*H*); 1.10 (d, $^3J_{H\text{-}H}$ = 6.18 Hz, 12H, ^{i}Pr-C*H*$_3$) ppm. ^{13}C NMR (101 MHz, C_6D_6, 298K): δ 91.6 ($^1J_{C\text{-}H}$ = 161 Hz, (^{i}PrO)$_2$*C*H$_2$); 69.0 ($^1J_{C\text{-}H}$ = 141 Hz, ^{i}Pr-*C*H); 23.0 ($^1J_{C\text{-}H}$ = 125 Hz, ^{i}Pr-*C*H$_3$) ppm.

Preparation of [(Cp*$_2$Sc][MeB(C$_6$F$_5$)$_3$] 3. A benzene (1.0g) solution of 158mg (0.31 mmol) B(C_6F_5)$_3$ was added to a solution of 100mg (0.30 mmol) of Cp*$_2$ScMe in benzene (1.0g; 20 mL screw cap vial) by pipet at room temperature (r.t.). The resulting solution was carefully layered with hexanes (~10mL), and the vial sealed and kept at r.t. overnight. Yellow block shaped crystals separated and were recovered by careful removal of the pale yellow mother liquor by pipet, washed with hexanes (2 mL, 3 times), and briefly dried under dynamic vacuum. Yield: 260mg (0.29 mmol), 98% **1**$_{Me}$*½C_6H_6. Note: The crystals partially lose lattice solvent upon prolonged drying under dynamic vacuum to give **3***1/6C_6H_6.

^{1}H NMR (400 MHz, C_6D_6, 298K): δ 7.20 (s, 3H, ½C_6H_6); 1.53 (s, 30H, C_5Me_5); 1.14 (br s, $\nu_{½}$ ~9Hz, 3H, B*Me*) ppm. ^{13}C‡^{1}H‡ NMR (101 MHz, C_6D_6, 298K): δ 149.8, 138.3, 137.8 (dm, C_6F_5); 128.4 (C_6H_6); 127.1 (C_5Me$_5$); 10.4 (C_5Me_5) ppm. ^{13}C resonances of C_{ispo} of C_6F_5 rings and BMe were not detected. ^{19}F NMR (376 MHz, C_6D_6, 298K): δ -133.7 (br s, $\nu_{½}$ ~163Hz, 6F, *o*-F); -161.7 (br t, $^{3}J_{F\text{-}F}$ = 21.2 Hz, 3F, *p*-F); -167.7 (br s, $\nu_{½}$ ~119Hz, 6F, *m*-F) ppm. ^{11}B NMR (128 MHz, C_6D_6, 298K): δ -14.0 (br s, $\nu_{½}$ ~145Hz) ppm. Analysis calcd./found for $C_{40}H_{34}BF_{15}Sc$, **3***1/6C_6H_6: C, 56.16/56.05; H, 4.01/4.09.

Calculation of K_{eq} in Scheme 1 for dissociation of $B(C_6F_5)_3$ from 2_{CIP}:

$$[\mathbf{2}_{CIP}] \rightleftharpoons [ScO_2C] + B()_3 \qquad K = \frac{[ScO_2C][B()_3]}{[2_{CIP}]}$$

Degree of B()3 dissociation from 2_{CIP} :

$$\alpha = \frac{[B()_3]}{[B()_3]+[2_{CIP}]} = \frac{[B()_3]}{[2_{CIP}]_0} \Rightarrow [B()_3] = \alpha \times [2_{CIP}]_0$$

$[2_{CIP}]_0$ = total [Sc]
From 19F NMR data: α ~0.06.

$$K = \frac{[ScO_2C][B()_3]}{[2_{CIP}]} = \frac{[B()_3]^2}{[2_{CIP}]_0 - [B()_3]} = \frac{\alpha^2[2_{CIP}]_0^2}{[2_{CIP}]_0 - \alpha[2_{CIP}]_0} = \frac{\alpha^2}{1-\alpha}[2_{CIP}]_0$$

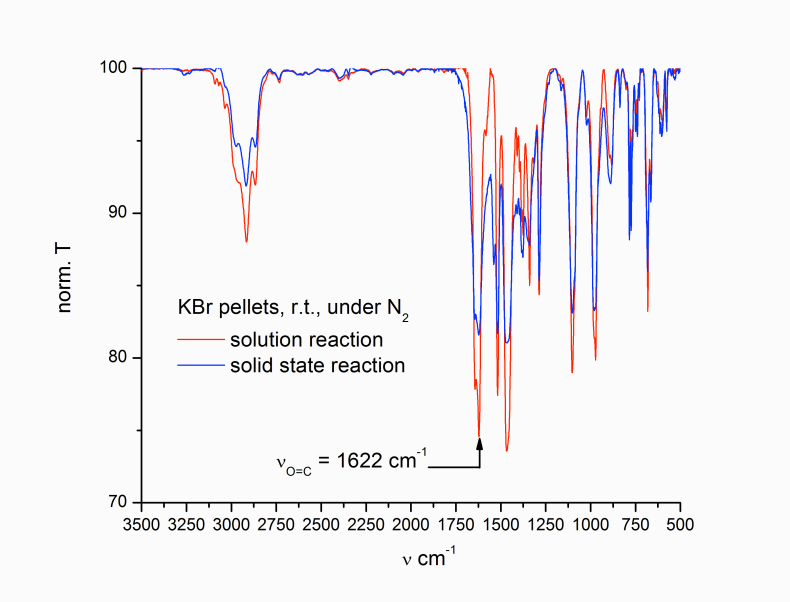

Figure S1. Overlay of baseline corrected IR spectra (KBr) taken from **2** prepared in solution (red) and from solid state reaction (blue), the carbonyl stretching band of **2** being highlighted.

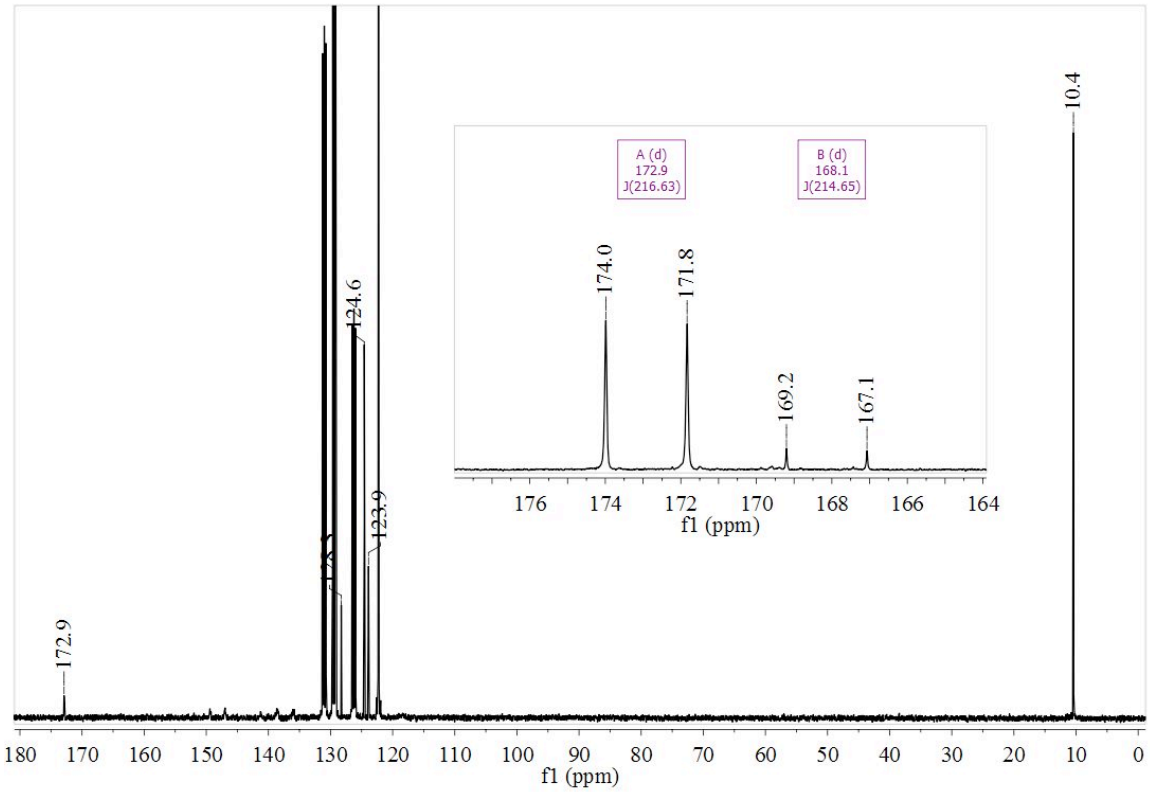

Figure S2. 101 MHz $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{2_{CIP}}$, C_6D_5Br, T = 298K. Inset: Carbonyl spectral region of 101 MHz ^{13}C NMR spectrum of ^{13}C labelled $\mathbf{2_{CIP}}$. Doublet resonance at 168.1 ppm corresponds to neutral Sc-formate species formed from partial, reversible borane dissociation.

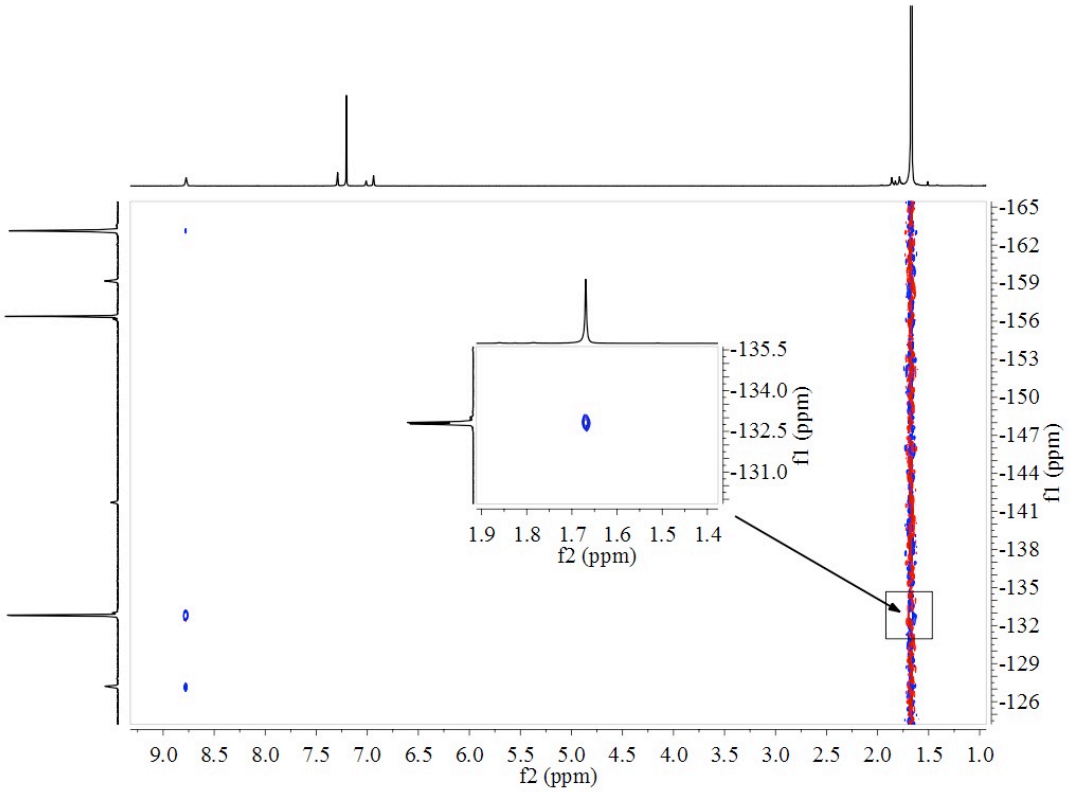

Figure S3. 400 MHz ^{1}H-^{19}F HOESY data, C_6D_5Br, T = 298K showing ^{1}H-^{19}F heteronuclear NOE cross-peaks between the formyl- and Cp* methyl-proton resonances and *ortho*-, *meta*-, and *para*-fluorine resonances for $\mathbf{2_{CIP}}$. Inset: Detected ^{1}H-^{19}F HOE cross-peak hidden under the streak caused by T1 noise of Cp* methyl proton resonance.

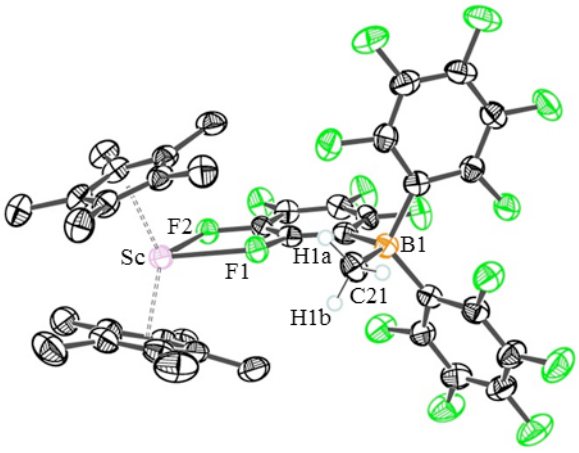

Figure S4. ORTEP representation of the molecular structure of **3** (thermal ellipsoids at 50% probability level). All hydrogen atoms except for B-CH_3, and co-crystallized C_6H_6 are omitted for clarity. Selected bond distances, Å: Sc-F1, 2.335(2); Sc-F2, 2.332(2); B-C21, 1.633(5); F1••H1a, 2.549(2); F1••H1b, 2.697(2).

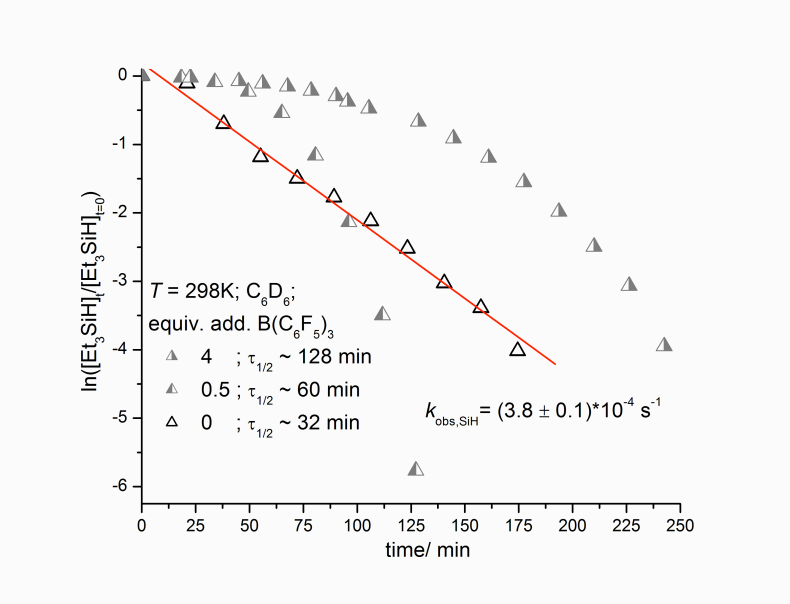

Figure S5. Semi-logarithmic plot of normalized silane concentration, $[Et_3SiH]_t/[Et_3SiH]_{t=0}$, vs. time as a function of additionally added $B(C_6F_5)_3$ co-catalyst; $\tau_{½} = 0.5*[Et_3SiH]_{t=0}$; $k_{obs,SiH}$ was determined by linear regression (red line; R = 0.995).

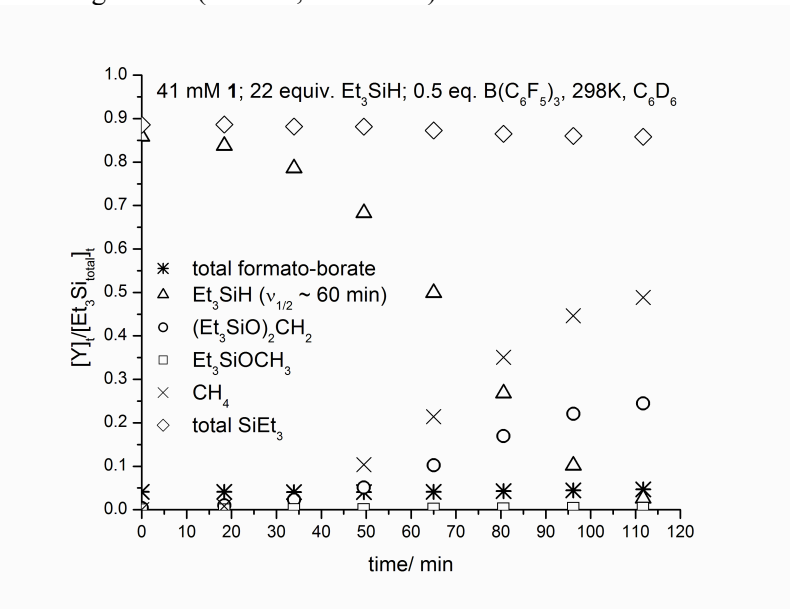

Figure S6. Plot of normalized reactant and product concentrations, $[Y]_t/[\text{total-}Et_3Si]_t$, vs. time; 0.5 equiv. additional $B(C_6F_5)_3$ co-catalyst; T = 298K, $P_{CO2} \geq 1$ atm.

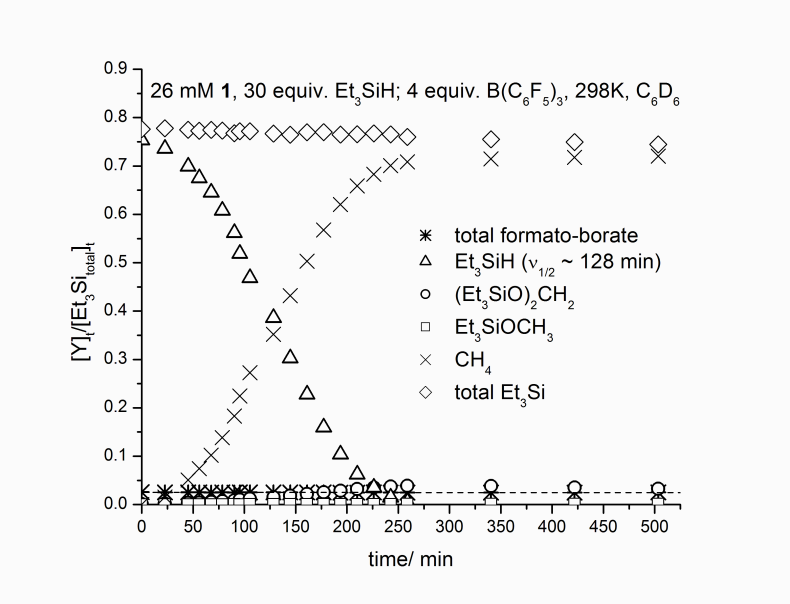

Figure S7. Plot of normalized reactant and product concentrations, $[Y]_t/[\text{total-Et}_3\text{Si}]_t$, vs. time; 4.0 equiv. additional $B(C_6F_5)_3$ co-catalyst; $T = 298$K, $P_{CO2} \geq 1$ atm.

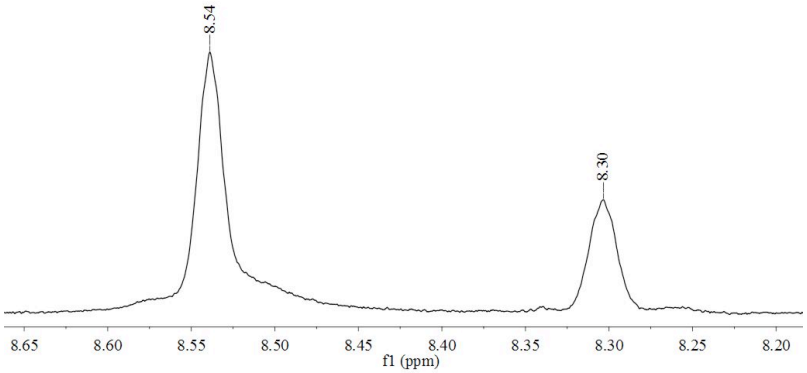

Figure S8. Low-field region of 400 MHz ^{1}H NMR spectrum: Characteristic resonances of formato-borate species formed after complete silane consumption in the presence of additional 4.0 equiv. $B(C_6F_5)_3$ co-catalyst: 8.54 ($^{dip}J_{H\text{-}F}$ ~1.7 Hz; Cp*, 1.68; $\Delta\ \delta F_{m\text{-}p}$ = 7.0), ~8.52 (**2**; $\nu_{½}$ ~25 Hz; Cp*, 1.68; $\Delta\ \delta F_{m\text{-}p}$ = 6.9), and 8.30 ($^{dip}J_{H\text{-}F}$ ~1.7 Hz; Cp*, 1.70; $\Delta\ \delta F_{m\text{-}p}$ = 7.4) ppm; d_6-benzene, $T = 298$K.

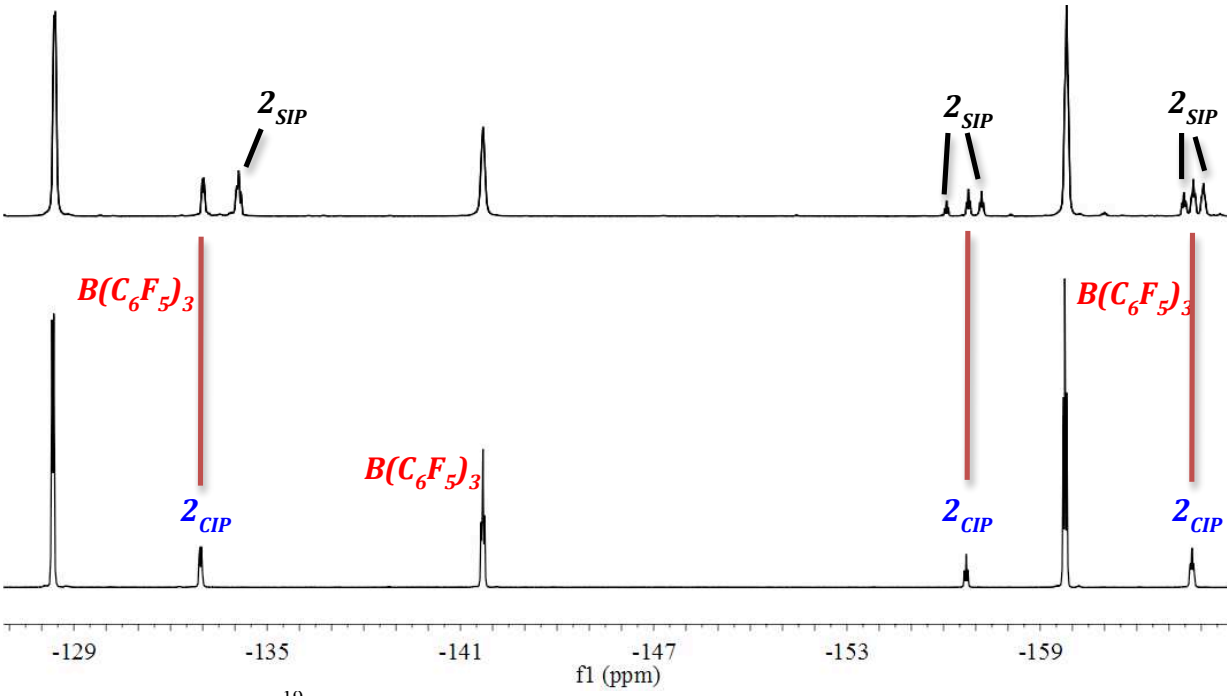

Figure S9. 376 MHz ^{19}F NMR spectrum before silane addition (bottom) and after complete silane consumption (top) in the presence of additional 4.0 equiv. $B(C_6F_5)_3$ co-catalyst. Resonances for $\mathbf{2_{CIP}}$ and $B(C_6F_5)_3$ are accompanied by the signals for the anions in $\mathbf{2_{SIP}}$ in the top spectrum.

Full Citation for reference 1: Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chemical Reviews* **2001**, *101*, 953.

Full Citation for reference 102: Gaussian 09, Revision **A.1**, 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, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

Cartesian geometries, electronic energies and Gibbs free energies for species in Figure 2.

CO_2

E = -188.504223
G = -188.510385

C	0.439817	0.000000	0.310995
O	-0.255930	0.000000	1.248979
O	1.136047	0.000000	-0.626636

Ion-pair $\mathbf{1}_{CIP}$

E = -1902.639676
G = -1902.121060

Sc	7.935312	7.089191	3.629685
C	6.212315	8.698337	2.912583
C	7.063672	9.378070	3.834934
C	6.901271	8.764730	5.115512
C	5.983979	7.682699	4.970075
C	5.536317	7.659987	3.612949
C	5.981000	9.116129	1.489456
C	7.786753	10.659977	3.538164
C	7.382390	9.318915	6.422315
C	5.471042	6.788877	6.063459
C	4.419471	6.807266	3.088674
C	10.223374	7.794555	4.237470
C	10.287402	7.154985	2.964567
C	9.950913	5.778250	3.143266
C	9.652482	5.574578	4.520483
C	9.819141	6.816969	5.199406
C	9.824817	6.969096	6.692432
C	10.754003	9.163683	4.541567
C	10.748455	7.784621	1.681018
C	10.045633	4.705425	2.098828
C	9.338926	4.262182	5.176383
F	7.686896	6.600287	1.280953
F	6.944292	5.060380	3.230566
C	6.543840	4.652153	1.974184
C	6.961346	5.491319	0.959955
C	6.638392	5.201449	-0.353633
F	7.030917	5.989743	-1.344356

C	5.891665	4.049306	-0.590279
F	5.571486	3.733278	-1.836598
C	5.495506	3.237911	0.474848
C	5.791858	3.505858	1.816292
F	4.804012	2.153384	0.147495
B	5.303045	2.661065	3.137229
C	3.948821	1.804198	2.857448
C	2.737664	2.477055	2.699743
C	1.517497	1.845296	2.493185
C	1.475511	0.457121	2.435082
C	2.654564	-0.262439	2.580219
C	3.854495	0.416250	2.780209
F	4.948436	-0.347299	2.889335
F	2.627176	-1.591554	2.520032
F	0.321886	-0.172415	2.239580
F	0.395887	2.549468	2.349163
F	2.717290	3.820039	2.729278
C	6.530469	1.802633	3.780144
C	7.595036	1.260568	3.062561
C	8.644222	0.555708	3.646124
C	8.649834	0.358314	5.021490
C	7.606399	0.870978	5.783473
C	6.582482	1.574396	5.155742
F	5.613501	2.042686	5.949467
F	7.606455	0.696048	7.103302
F	9.644423	-0.304453	5.601846
F	9.639307	0.073951	2.904255
F	7.648109	1.396434	1.729023
H	5.011218	3.512637	3.954520
H	10.733830	6.518599	7.110442
H	8.977070	6.466597	7.169040
H	9.811828	8.015269	7.001453
H	11.833692	9.109958	4.731693
H	10.296818	9.601625	5.431636
H	10.610389	9.860986	3.712659
H	11.825184	7.629879	1.536903
H	10.576945	8.864968	1.669396
H	10.245608	7.358451	0.807815
H	11.044570	4.251799	2.117170
H	9.895105	5.093172	1.087571
H	9.331508	3.893709	2.261224
H	10.258284	3.797506	5.555001
H	8.878840	3.552148	4.485446
H	8.664951	4.375787	6.030795
H	7.072783	11.489916	3.461701
H	8.332509	10.624447	2.589313

H	8.499842	10.919725	4.322331
H	6.661253	10.056881	6.796495
H	8.344131	9.829269	6.335169
H	7.477590	8.548083	7.189726
H	4.529418	7.176388	6.472607
H	6.174868	6.713670	6.897359
H	5.267826	5.774984	5.704985
H	3.455199	7.261471	3.349192
H	4.415735	5.798992	3.510666
H	4.439577	6.713645	2.000149
H	5.291122	9.968502	1.449670
H	5.535951	8.317734	0.890774
H	6.903811	9.430093	0.991101

CO_2 adduct

E = -2091.146058
G = -2090.617900

C	0.465985	-3.589686	-0.772720
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C	0.418614	-3.404109	1.560336
C	-0.024638	-4.714112	1.689307
C	-0.223454	-5.479132	0.545237
C	0.020564	-4.908089	-0.695638
B	1.179141	-1.224013	0.355124
C	1.357332	-0.556599	-1.128721
C	0.505134	0.391030	-1.665880
C	0.617775	0.936392	-2.938120
C	1.680191	0.552172	-3.741942
C	2.595692	-0.373477	-3.249316
C	2.415072	-0.900649	-1.975604
F	-0.570800	0.854097	-0.931549
F	-0.281241	1.816096	-3.389701
F	1.818398	1.063990	-4.957935
F	3.617089	-0.749651	-4.006652
F	3.301379	-1.807107	-1.573199
F	0.574769	-2.713020	2.697724
F	-0.271236	-5.238242	2.887571
F	-0.654995	-6.731898	0.639152
F	-0.183933	-5.618481	-1.802720
F	0.648265	-3.116570	-2.015737
C	2.539394	-0.957505	1.220127
C	2.779765	0.314100	1.731977
C	3.887448	0.660751	2.494219

C	4.839356	-0.311452	2.775687
C	4.656058	-1.598394	2.284445
C	3.527234	-1.893987	1.522852
F	1.893956	1.305738	1.487723
F	4.042137	1.902996	2.952747
F	5.911031	-0.012706	3.501130
F	5.562873	-2.535194	2.544111
F	3.427745	-3.150812	1.084555
O	-1.572447	1.069533	1.728605
C	-0.903448	0.640496	2.595764
O	-0.313359	0.248209	3.510119
Sc	-2.421196	2.064056	-0.192670
C	-0.756909	3.907573	-0.347920
C	-1.852567	4.258255	-1.194224
C	-2.990289	4.488796	-0.365504
C	-2.613985	4.232834	0.985222
C	-1.226154	3.899934	0.994919
C	-4.229884	5.202661	-0.811782
C	-1.781822	4.584985	-2.658197
C	0.678242	3.754774	-0.757692
C	-0.364726	3.778414	2.215723
C	-3.457667	4.468783	2.204961
C	-4.869726	1.660472	-0.429480
C	-4.276216	1.427010	-1.707878
C	-3.425660	0.288738	-1.591392
C	-3.476910	-0.170945	-0.245414
C	-4.357342	0.688528	0.476467
C	-6.051231	2.536441	-0.138230
C	-4.653350	2.077645	-3.006630
C	-2.738097	-0.408469	-2.727451
C	-2.820957	-1.417898	0.266227
C	-4.806537	0.523074	1.899303
H	-3.327265	-2.303736	-0.136366
H	-1.767563	-1.490934	-0.017148
H	-2.874221	-1.490835	1.355269
H	-3.434494	-1.098924	-3.220543
H	-2.384960	0.287986	-3.492595
H	-1.886879	-1.005015	-2.390745
H	-5.768272	-0.003797	1.943423
H	-4.097437	-0.061668	2.490523
H	-4.947144	1.485261	2.402049
H	-6.957941	1.919703	-0.088394
H	-5.971247	3.055251	0.821608
H	-6.215434	3.284629	-0.914296
H	-5.410475	1.477806	-3.528044
H	-5.077945	3.074006	-2.865133

H	-3.800299	2.170149	-3.685325
H	-3.218672	3.772571	3.015193
H	-3.299630	5.480522	2.599909
H	-4.525059	4.371786	1.990890
H	-4.592535	4.860242	-1.783881
H	-5.045525	5.116119	-0.092582
H	-4.008607	6.272975	-0.917922
H	-0.946583	4.087606	-3.153050
H	-2.696370	4.306168	-3.189043
H	-1.647648	5.665632	-2.798509
H	0.779710	3.590679	-1.832268
H	1.234874	4.670296	-0.520510
H	1.179995	2.934770	-0.237286
H	0.487971	3.112361	2.066008
H	0.047589	4.760901	2.479304
H	-0.927384	3.437078	3.090145
H	0.289174	-0.609535	0.913801

TS1

E = -2091.140145
G = -2090.611176

C	3.530432	-7.677168	0.104432
C	3.610534	-6.863441	1.235608
C	3.060837	-7.427797	2.389405
C	2.481837	-8.688441	2.442380
C	2.432264	-9.460905	1.286906
C	2.960800	-8.949084	0.109936
B	4.267182	-5.380597	1.298282
C	4.508191	-4.701184	-0.161855
C	3.584511	-3.918250	-0.834752
C	3.753196	-3.422414	-2.120406
C	4.938233	-3.683919	-2.793252
C	5.917163	-4.444012	-2.161811
C	5.684165	-4.934086	-0.880915
F	2.395458	-3.598282	-0.235368
F	2.802341	-2.689405	-2.700989
F	5.132536	-3.209059	-4.014684
F	7.052473	-4.706387	-2.793027
F	6.639273	-5.699269	-0.356807
F	3.069450	-6.726027	3.526617
F	1.968456	-9.156194	3.574976
F	1.878905	-10.665151	1.307934
F	2.914666	-9.671324	-1.004647

F	4.009451	-7.268192	-1.076253
C	5.551208	-5.214112	2.265800
C	5.985481	-3.933900	2.604531
C	7.067798	-3.667904	3.431922
C	7.785254	-4.733499	3.962377
C	7.402745	-6.032432	3.649254
C	6.308073	-6.248619	2.816216
F	5.330413	-2.867516	2.111222
F	7.419441	-2.417373	3.717148
F	8.825663	-4.512869	4.754028
F	8.089409	-7.056844	4.142226
F	6.019720	-7.523537	2.546281
O	1.623629	-3.391349	2.366832
C	2.576893	-3.801459	2.987370
O	3.192324	-3.903328	3.982986
Sc	0.548200	-2.337083	0.748257
C	2.202384	-0.493389	0.469684
C	1.059114	-0.156392	-0.318662
C	-0.027048	0.090799	0.570454
C	0.425856	-0.154345	1.900061
C	1.812246	-0.485563	1.835861
C	-1.292454	0.799598	0.193755
C	1.057257	0.133730	-1.792402
C	3.610472	-0.626898	-0.030164
C	2.730390	-0.607293	3.013328
C	-0.343237	0.079987	3.168689
C	-1.917144	-2.731533	0.631661
C	-1.401687	-2.934336	-0.684610
C	-0.543148	-4.071990	-0.646574
C	-0.521357	-4.567063	0.686954
C	-1.350611	-3.723946	1.482155
C	-3.073236	-1.856888	1.016289
C	-1.860514	-2.267846	-1.948463
C	0.085428	-4.723399	-1.843530
C	0.141150	-5.829341	1.140112
C	-1.686794	-3.923204	2.931554
H	-0.482134	-6.697283	0.890061
H	1.113227	-5.980877	0.665526
H	0.293188	-5.844292	2.221862
H	-0.650345	-5.345443	-2.369435
H	0.461390	-3.993151	-2.565760
H	0.914871	-5.378152	-1.565442
H	-2.560487	-4.578025	3.044111
H	-0.864257	-4.386224	3.483396
H	-1.928905	-2.978581	3.427938
H	-3.977095	-2.470691	1.120987

H	-2.924214	-1.351147	1.975023
H	-3.286887	-1.097416	0.263631
H	-2.616791	-2.885656	-2.450091
H	-2.317425	-1.293175	-1.764554
H	-1.044055	-2.126295	-2.663006
H	-0.076676	-0.639742	3.949344
H	-0.135655	1.078978	3.573265
H	-1.423229	0.015336	3.013571
H	-1.712183	0.449944	-0.752295
H	-2.062873	0.713893	0.961227
H	-1.082000	1.870092	0.069768
H	1.746232	-0.508685	-2.345394
H	0.063647	0.010136	-2.230575
H	1.363603	1.171384	-1.979480
H	3.642095	-0.815232	-1.105335
H	4.159507	0.307358	0.144061
H	4.169795	-1.418714	0.474506
H	3.630758	-1.180053	2.782082
H	3.062262	0.389264	3.332456
H	2.245293	-1.070077	3.877244
H	3.370149	-4.641326	1.879436

Intermediate

E = -2091.181193
G = -2090.656147

C	3.034853	-4.645013	-0.220734
C	2.355461	-3.422469	-0.139325
C	0.988387	-3.469486	-0.442150
C	0.333363	-4.636895	-0.810169
C	1.050304	-5.828967	-0.866136
C	2.409556	-5.836196	-0.564945
B	3.072608	-2.089155	0.262672
C	4.528920	-1.804119	-0.237456
C	4.963316	-2.168117	-1.518967
C	6.246694	-1.913135	-1.983462
C	7.162287	-1.286924	-1.142161
C	6.781720	-0.915530	0.144513
C	5.483264	-1.167349	0.567063
F	4.124650	-2.761660	-2.364738
F	6.606921	-2.258922	-3.209650
F	8.388653	-1.045971	-1.563401
F	7.655360	-0.327296	0.946661
F	5.172837	-0.798351	1.806925

F	0.259335	-2.356104	-0.412045
F	-0.957482	-4.627954	-1.103821
F	0.443031	-6.949877	-1.204023
F	3.088693	-6.971732	-0.610735
F	4.332813	-4.708007	0.065036
C	2.331294	-1.043581	1.157908
C	2.469009	0.338225	0.965371
C	1.807702	1.279782	1.740431
C	0.980590	0.850449	2.773460
C	0.821731	-0.510962	3.015164
C	1.480632	-1.424980	2.204714
F	3.235580	0.801798	-0.019841
F	1.953796	2.574233	1.507499
F	0.348880	1.731552	3.522124
F	0.045614	-0.918948	4.007213
F	1.296100	-2.714471	2.479635
O	-2.019563	1.341419	-1.987663
C	-1.122367	1.094965	-1.132050
O	-1.226519	1.486590	0.067923
Sc	-3.192591	2.394741	-0.443901
C	-2.750055	4.310905	-1.989299
C	-3.942636	4.642999	-1.288278
C	-3.607734	4.815706	0.090485
C	-2.211411	4.575589	0.234661
C	-1.679886	4.280997	-1.053406
C	-4.489861	5.410558	1.147899
C	-5.248694	4.993724	-1.941550
C	-2.621418	4.120925	-3.471714
C	-0.232442	4.097187	-1.392252
C	-1.413633	4.704336	1.499693
C	-4.850762	1.636187	1.277229
C	-5.582949	1.797068	0.061799
C	-5.087454	0.847163	-0.876057
C	-4.082381	0.070900	-0.228766
C	-3.931686	0.564177	1.095466
C	-5.145328	2.297549	2.592891
C	-6.832251	2.608696	-0.106258
C	-5.596213	0.619432	-2.270680
C	-3.400069	-1.133730	-0.801302
C	-3.040386	-0.010112	2.155424
H	-3.973459	-2.043845	-0.581196
H	-3.292592	-1.065765	-1.886697
H	-2.402067	-1.279745	-0.376838
H	-6.329817	-0.196931	-2.300178
H	-6.090261	1.507920	-2.675500
H	-4.786340	0.351119	-2.956775

H	-3.544730	-0.819834	2.699125
H	-2.122485	-0.420908	1.727504
H	-2.751309	0.742841	2.894815
H	-5.723189	1.627632	3.243244
H	-4.234353	2.561034	3.141233
H	-5.731328	3.210308	2.469441
H	-7.704663	2.028194	0.222771
H	-6.820640	3.526639	0.486838
H	-7.009175	2.887656	-1.147362
H	-0.594373	3.980735	1.534762
H	-0.968988	5.704120	1.590936
H	-2.030567	4.546694	2.389790
H	-5.546531	5.179262	0.992807
H	-4.220034	5.070911	2.151258
H	-4.400214	6.505217	1.146479
H	-5.563906	4.251643	-2.683270
H	-6.055163	5.093003	-1.213032
H	-5.168628	5.954027	-2.467373
H	-3.592845	3.935484	-3.939100
H	-2.199048	5.015156	-3.948255
H	-1.971175	3.275618	-3.715604
H	-0.096868	3.405416	-2.230102
H	0.219558	5.051778	-1.691975
H	0.340997	3.718583	-0.542830
H	-0.230188	0.525792	-1.438896

TS2

E = -2091.170317
G = -2090.640451

Sc	5.452681	8.119723	3.548359
C	7.286080	6.476852	3.823163
C	6.354984	6.237829	4.876443
C	6.385247	7.357270	5.755815
C	7.307684	8.307365	5.223642
C	7.862420	7.759360	4.031628
C	4.527593	10.412108	3.429154
C	4.253000	9.972904	4.756820
C	3.349729	8.871888	4.676191
C	3.043618	8.656818	3.299945
C	3.756591	9.618370	2.532388
C	3.618673	9.857553	1.062107
C	7.702680	5.497318	2.771718
C	2.025831	7.686486	2.778281

C	5.592892	4.966305	5.108155
C	2.643770	8.208014	5.823839
C	5.774922	7.372718	7.124928
C	4.608857	10.732185	5.999321
C	7.821300	9.541457	5.907709
C	5.379274	11.584686	3.035352
C	8.941281	8.387940	3.201312
O	6.212980	8.298664	1.562819
C	5.703115	7.366814	0.865394
O	4.902111	6.514344	1.321807
B	4.045603	4.699462	-0.294990
C	2.619453	5.366717	-0.417205
C	2.452609	6.658754	-0.929716
C	1.216976	7.272659	-1.077854
C	0.065371	6.577112	-0.722178
C	0.172529	5.281755	-0.230723
C	1.430559	4.705469	-0.088252
C	4.277353	3.530498	0.739872
C	3.730692	3.553025	2.029442
C	3.857375	2.504051	2.930601
C	4.557355	1.361022	2.557127
C	5.112573	1.284513	1.285890
C	4.964819	2.355463	0.410521
C	5.076739	4.902345	-1.478103
C	6.461910	4.834653	-1.288283
C	7.386938	4.980208	-2.313654
C	6.935714	5.174366	-3.614952
C	5.568863	5.220466	-3.864567
C	4.674929	5.088218	-2.807686
F	3.515042	7.367150	-1.309189
F	1.123701	8.505256	-1.556595
F	-1.120651	7.142969	-0.856514
F	-0.920344	4.606236	0.095122
F	1.450145	3.451571	0.360319
F	3.034898	4.605530	2.442791
F	3.308957	2.576547	4.136469
F	4.686565	0.354927	3.403589
F	5.769421	0.194454	0.914886
F	5.494502	2.192472	-0.800969
F	6.954579	4.618542	-0.072932
F	8.687908	4.923348	-2.064779
F	7.798889	5.305578	-4.605776
F	5.129077	5.386075	-5.103741
F	3.383184	5.115161	-3.130896
H	2.343656	7.232290	1.837638
H	4.834122	6.818260	7.162476

H	6.120281	11.828511	3.802376
H	8.533323	4.876738	3.133130
H	1.842234	6.873915	3.485816
H	1.065476	8.190058	2.604814
H	3.340538	8.947786	0.528440
H	2.835584	10.601119	0.864450
H	4.545623	10.230753	0.619004
H	8.817364	8.163342	2.138931
H	6.890572	4.826955	2.484771
H	8.049960	5.999086	1.865366
H	4.600847	5.143530	5.535446
H	6.127384	4.304877	5.802638
H	5.457460	4.411916	4.177124
H	2.575638	7.120954	5.706404
H	1.614892	8.580867	5.909901
H	3.138280	8.406701	6.776448
H	4.655347	10.096268	6.885601
H	5.564342	11.253019	5.909511
H	3.845332	11.496426	6.196614
H	4.768738	12.484098	2.881981
H	5.918128	11.398458	2.100932
H	7.206467	9.819527	6.765269
H	5.583808	8.382928	7.492301
H	7.873237	10.407940	5.239473
H	8.838629	9.370830	6.282453
H	6.455041	6.895623	7.843288
H	9.931823	8.026042	3.506213
H	8.948972	9.476837	3.307249
H	5.994174	7.329150	-0.196636

Product 2_{CIP}

E = -2091.197611
G = -2090.666398

Sc	0.844505	2.260167	2.607002
C	2.323394	0.323511	2.956826
C	1.625166	0.536114	4.182613
C	2.064013	1.776069	4.731576
C	2.986163	2.361799	3.813773
C	3.154559	1.454997	2.721563
C	0.068160	4.596571	2.481798
C	-0.268590	4.153458	3.794164
C	-1.212827	3.091232	3.670294
C	-1.490099	2.909605	2.279478

C	-0.713329	3.852947	1.548687
C	-0.776409	4.113733	0.074575
C	2.265867	-0.933118	2.142905
C	-2.497182	1.953493	1.708133
C	0.717722	-0.456600	4.852151
C	-1.937872	2.406876	4.793607
C	1.808449	2.226094	6.138055
C	0.098028	4.875803	5.055268
C	3.787715	3.613125	4.033687
C	0.954448	5.762741	2.148094
C	4.109528	1.632585	1.577215
O	0.897601	1.596175	0.636245
C	0.686588	0.910348	-0.386736
O	-0.005785	-0.152293	-0.360174
B	-0.333378	-1.126059	-1.542372
C	-1.897655	-0.812704	-1.904212
C	-2.307539	0.495816	-2.152967
C	-3.611850	0.869457	-2.444924
C	-4.593181	-0.112721	-2.513957
C	-4.238896	-1.437004	-2.293295
C	-2.915699	-1.760991	-1.997377
C	-0.124070	-2.602281	-0.867361
C	-0.622817	-2.876827	0.408584
C	-0.475918	-4.100021	1.051594
C	0.184746	-5.136932	0.404479
C	0.678115	-4.925057	-0.875297
C	0.513501	-3.680814	-1.480251
C	0.690146	-0.855407	-2.795437
C	2.070828	-0.825252	-2.592267
C	3.011481	-0.661122	-3.599905
C	2.575339	-0.530351	-4.913112
C	1.212599	-0.565751	-5.178221
C	0.306340	-0.725457	-4.131374
F	-1.394819	1.485980	-2.148257
F	-3.924686	2.143506	-2.663237
F	-5.848534	0.211507	-2.789844
F	-5.164951	-2.385977	-2.362973
F	-2.666398	-3.060528	-1.820430
F	-1.315009	-1.946475	1.079632
F	-0.966834	-4.286448	2.274595
F	0.337601	-6.311592	1.000312
F	1.304308	-5.907692	-1.513268
F	0.998409	-3.578974	-2.722304
F	2.556860	-0.972647	-1.346932
F	4.310784	-0.631822	-3.322326
F	3.448135	-0.370682	-5.896565

F	0.782423	-0.444864	-6.427945
F	-0.979082	-0.769047	-4.487313
H	-2.248364	1.656031	0.687177
H	0.775436	2.057649	6.454985
H	1.752949	5.896562	2.883716
H	2.888004	-1.710022	2.605418
H	-2.581753	1.037538	2.300865
H	-3.494498	2.410626	1.680842
H	-1.198004	3.271315	-0.475387
H	-1.414032	4.983009	-0.129698
H	0.208240	4.330823	-0.351645
H	3.797639	1.069668	0.694253
H	1.251567	-1.333475	2.069463
H	2.637079	-0.786174	1.127950
H	0.021058	0.027369	5.542184
H	1.297284	-1.183781	5.435327
H	0.128380	-1.029698	4.129466
H	-2.164885	1.361083	4.564803
H	-2.895961	2.902228	4.996699
H	-1.364289	2.424170	5.723874
H	-0.087753	4.274841	5.946404
H	1.144695	5.193302	5.073522
H	-0.509857	5.785215	5.147978
H	0.379204	6.697453	2.124652
H	1.421503	5.655262	1.164019
H	3.275797	4.318286	4.693682
H	2.038449	3.282406	6.284211
H	4.004886	4.134851	3.096262
H	4.754479	3.381024	4.498613
H	2.447373	1.658756	6.827224
H	5.112354	1.279687	1.848651
H	4.211434	2.682360	1.282730
H	1.112833	1.242725	-1.339893