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Supporting Information for

Selective Reduction of Carbon Dioxide to Bis(silyl)acetal Catalyzed by a PBP-Supported Nickel Complex

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General Methods

All manipulations were carried out using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried and degassed prior to use. *n*-Pentane was distilled over sodium and stored under Na/K alloy. Benzene-***d***$_6$ (C_6D_6) was distilled under argon over sodium/benzophenone and stored under 3 Å activated molecular sieves. Solution NMR spectra were acquired on Bruker AMX-300 and DRX-400 spectrometers at 298 K unless otherwise specified. ^{1}H and ^{13}C chemical shifts were referenced to the residual solvent peak. ^{31}P NMR spectra were referenced to an external 85% solution of H_3PO_4. ^{19}F NMR spectra were referenced to an external standard of $CFCl_3$. ^{11}B NMR spectra were referenced to an external standard of $BF_3{\cdot}Et_2O$. ^{29}Si chemical shifts were referenced to an external standard of $Si(CH_3)_4$. Elemental analysis was carried out with a LECO TruSpec CHN elementary analyser. Infra-red data (Nujol on NaCl plates) were measured on a Bruker Vector 22 instrument. *Tris*-(pentafluorophenyl)borane was purchased from TCI and sublimed at 100 ºC under high static vacuum. Triethylsilane and dimethylphenylsilane were distilled from CaH_2 and stored under 3 Å activated molecular sieves. All other commercially available reagents were purchased from Sigma-Aldrich, TCI or Alfa Aesar and used as received. Flash column chromatography was carried out on Merck Silica Gel 60 (0.063-0.200 mm), and the process was monitored by using TLC precoated silica gel plates (Merck Silica Gel 60 F254). Spots were visualized by means of UV light (254 nm) or using a solution of potassium permanganate. Carbon dioxide and ^{13}C-labeled carbon dioxide (99.05% ^{13}C) were supplied by Air Liquide and Euriso-top, respectively, and used as received. Compound **2** was prepared according to the procedure previously described in the literature.[1]

Synthesis and characterization of 4

A J. Young valve NMR tube containing a solution of **2** (26 mg, 0.053 mmol) in C_6D_6 (0.5 mL) was charged with CO_2 (4 bar). The NMR tube was shaken at r.t., and instantaneous CO_2 insertion was confirmed by ^{31}P and ^{1}H NMR analysis. In a glovebox, a solution of $B(C_6F_5)_3$ (30 mg, 0.058 mmol, 1.1 eq) in C_6D_6 (0.2 mL) was added to the tube. Instantaneous formation of **4** was confirmed again by NMR. The mixture was filtered via cannula to a previously flame-dried Schlenk flask. The solvent was removed under vacuum, and pentane (2 mL) was added to remove the remaining benzene; the mixture was vigorously stirred until a powdery suspension was observed, after which the mixture was dried in vacuo. Then, the solid was washed with pentane (2 x 2 mL) at -20ºC and then it was dried under vacuum, affording **4** as a yellowish solid (48.9 mg, 0.046 mmol, 88%).

^{1}H-NMR (400 MHz, C_6D_6, 25 ºC): δ 0.99 (vt, 36 H, $^{3}J_{HP}$= 6.8 Hz, ^{t}Bu), 3.31 (vt, 4 H, $^{2}J_{HP}$ = 2.1 Hz, C***H***$_2$), 6.81 (dd, 2 H, $^{3}J_{HH}$ = 5.7 Hz, $^{4}J_{HH}$ = 3.1 Hz, arom C***H***), 7.09 (dd, 2 H, $^{3}J_{HH}$ = 5.7 Hz, $^{4}J_{HH}$ = 3.1 Hz, arom C***H***), 8.45 (s, 1 H, ***H***COO) ppm. **^{13}C{^{1}H}-NMR** (100 MHz, C_6D_6, 25 ºC): δ 29.1 (t, $^{2}J_{CP}$ = 2.5 Hz, (***C***H)$_3$C), 35.0 (t, $^{1}J_{CP}$ = 5.4 Hz, (CH)$_3$***C***), 39.0 (t, $^{1}J_{CP}$ = 19.2 Hz, ***C***H$_2$), 109.1 (arom***C***H), 119.6 (arom ***C***H), 137.6 (dm, $^{1}J_{CF\sim}$ 246 Hz, ***C***$_6$F$_5$), 138.6 (t, $^{3}J_{CP}$ = 7.3 Hz, arom***C***$_q$), 140.3 (dm, $^{1}J_{CF\sim}$ 259 Hz, ***C***$_6$F$_5$), 148.8 (dm, $^{1}J_{CF\sim}$ 245 Hz, ***C***$_6$F$_5$), 173.2 (H***C***OO) ppm**.** ^{13}C resonances of C_{ipso} of C_6F_5 rings were not detected. **^{31}P{^{1}H}-NMR** (161 MHz, C_6D_6, 25ºC) δ 87.7 (s) ppm. **^{11}B{^{1}H}-NMR** (128 MHz, C_6D_6, 25 ºC): δ -1.4 (bs, ***B***$(C_6F_5)_3$), 33.5 (bs, boryl) ppm. **^{19}F-NMR** (376 MHz, C_6D_6, 25 ºC): -164.5 (td, $^{3}J_{FF}$ = 24 Hz, $^{4}J_{FF}$ = 3.8 Hz, meta C-***F***), -157.8 (t, $^{3}J_{FF}$ = 19 Hz, para C-***F***), -132.7 (d, $^{3}J_{FF}$ = 22.6 Hz, ortho C-***F***) ppm. **IR** ν(Nujol) 1643 cm^{-1} Anal.Calcd.for $C_{43}H_{45}B_2F_{15}N_2NiO_2P_2$: C, 49.23; H, 4.32; N, 2.67. Found: C, 49.14; H, 4.18; N, 2.85.

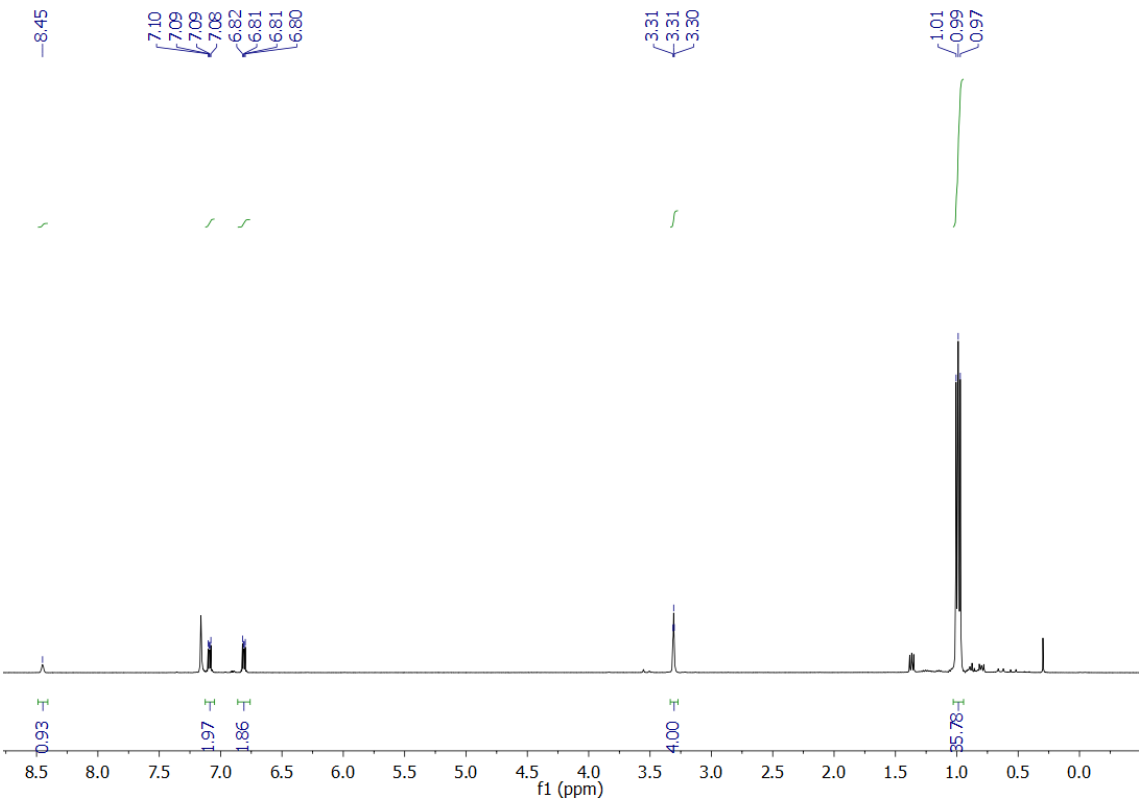


Figure S1. ^{1}H NMR spectrum of **4**

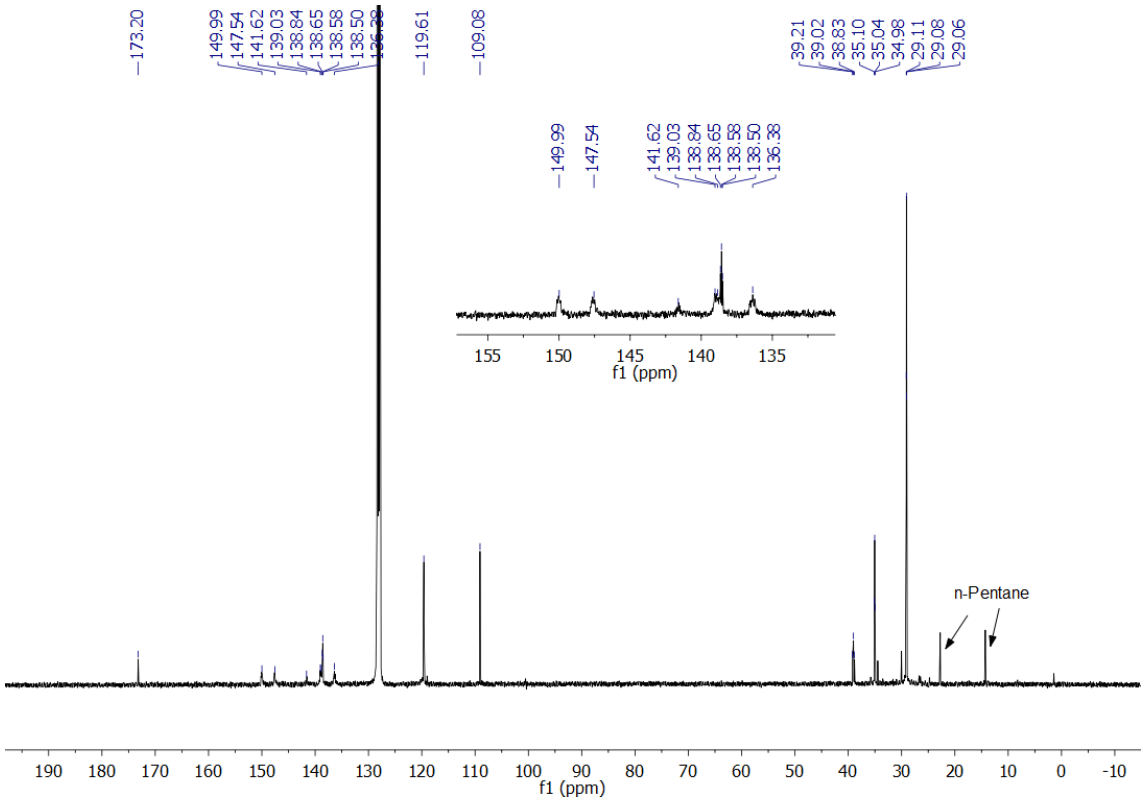


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **4**

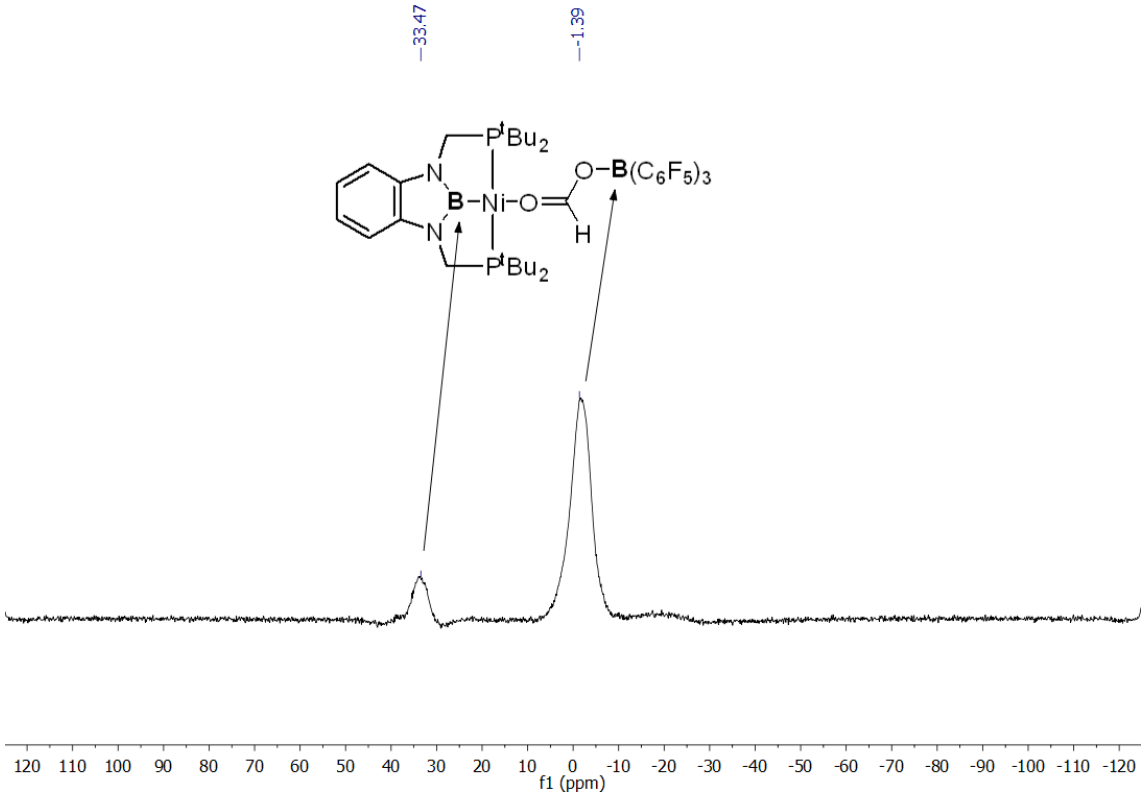


Figure S3. $^{11}B\{^{1}H\}$ NMR spectrum of **4**

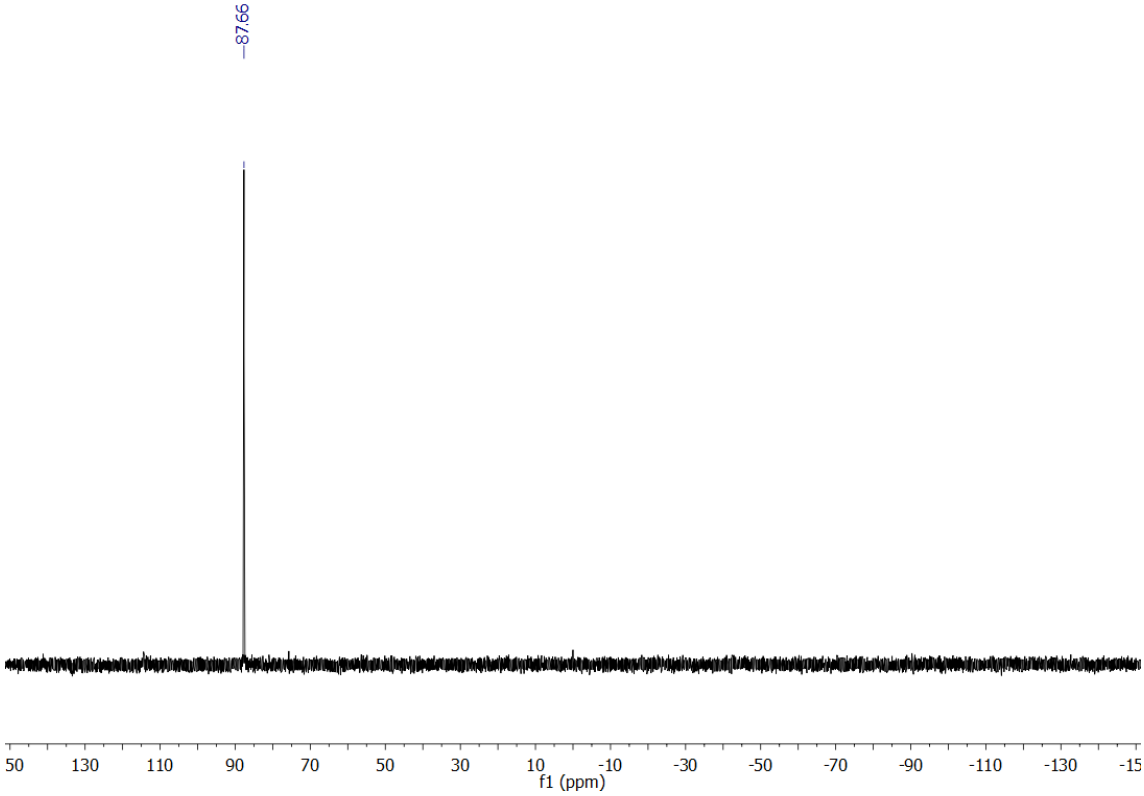


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **4**

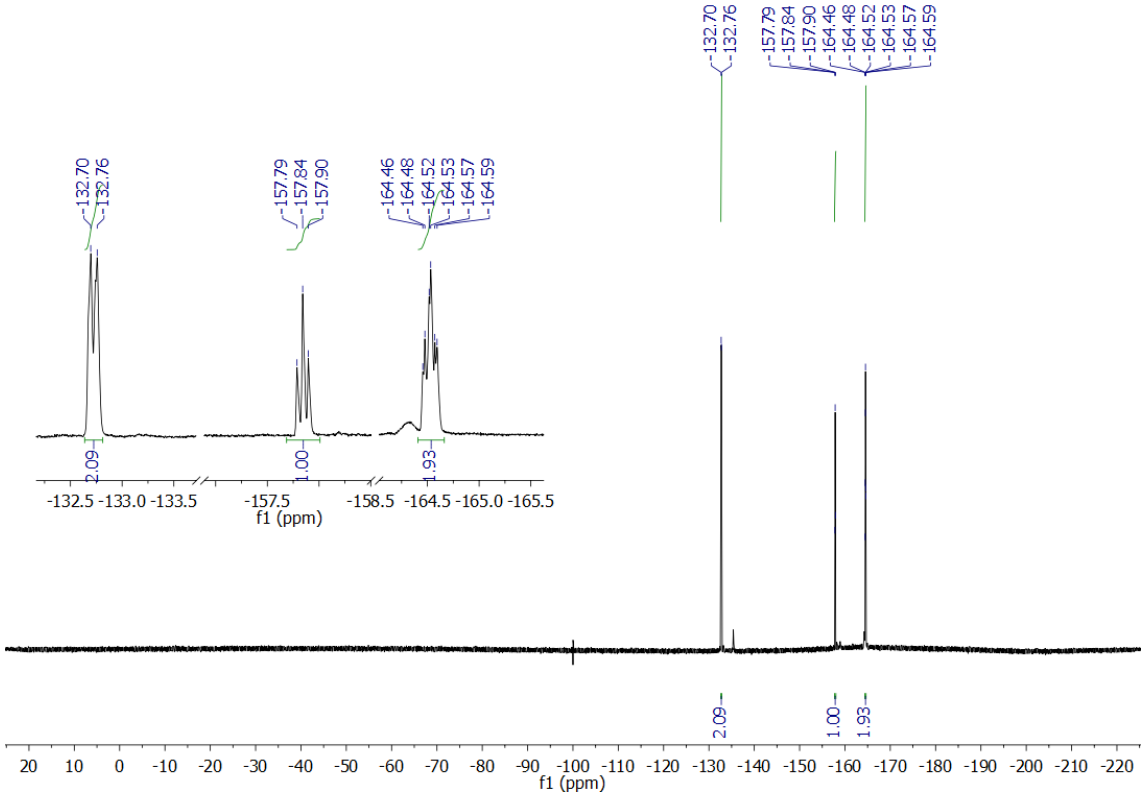


Figure S5. ^{19}F NMR spectrum of **4**.

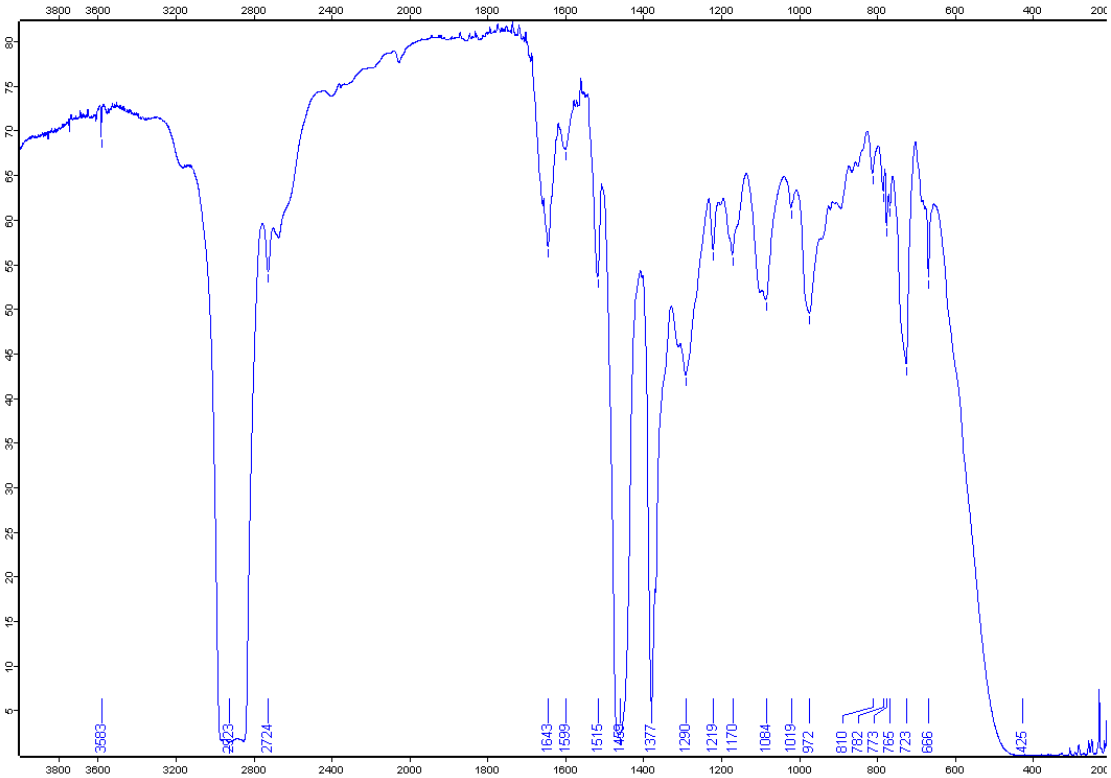


Figure S6. IR spectrum of **4**.

X-Ray Structural Characterization

A single crystal of suitable size, coated with dry perfluoropolyether, was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173(2) K] to the goniometer head. Data collection was performed on a Bruker-Nonius X8APEX-II CCD diffractometer, using monochromatic radiation λ(Mo Kα1) = 0.71073 Å, by means of ω and φ scans. The data were reduced (SAINT)[2] and corrected for Lorentz polarization effects and absorption by multiscan method applied by SADABS.[3] The structures were solved by direct methods (SHELX97)[4] and refined against all F2 data by full-matrix least-squares techniques (SHELXTL-6.12).[5] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters. CCDC-1428727 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

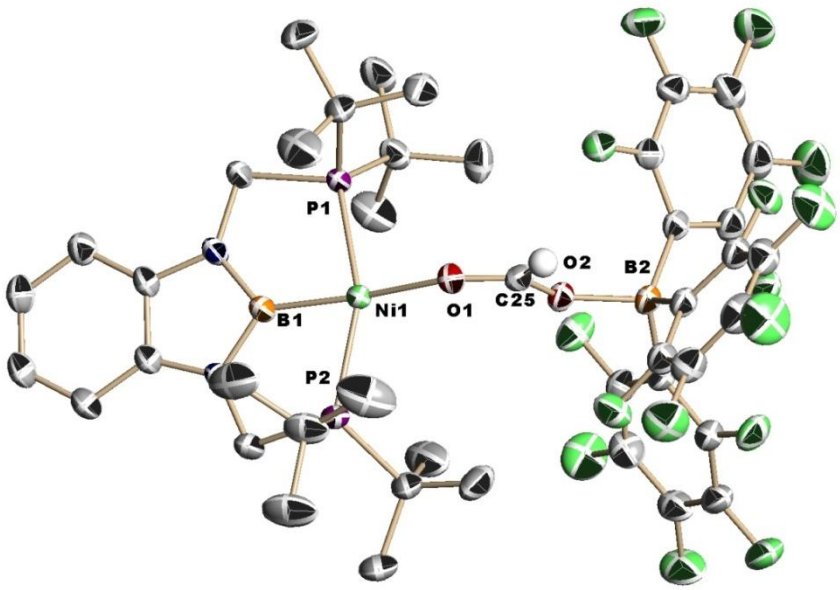


Figure S7. X-Ray structure of **4**

Table S1. Crystal data and structure refinement

Empirical formula	$C_{43}H_{45}B_2F_{15}N_2NiO_2P_2$
Formula weight	1049.08
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	I2/a
Unit cell dimensions	a = 23.4136 (16) Å α = 90^0
	b = 11.6676 (8) Å β = 102.822(4)º
	c = 35.146 (3) Å γ = 90^0
Volume	9361.8 (12) $Å^3$
Z	8
Density (calculated)	1.489 Mg m^{-3}
Absorption coefficient	0.58 mm^{-1}
F(000)	4288
Crystal size	0.22 × 0.11 × 0.03 mm
Theta range for data collection	2.4–30.3°
Index ranges	-33<=h<=32, -16<=k<=15, -38<=l<=50
Reflections collected	114841
Independent reflections	14186 (R_{int} = 0.042)
Completeness to theta =30.51^0	99.1%
Absorption correction	Multi-scan (*SADABS*, Bruker (2001))
Max. and min. transmission	0.9828 and 0.8828
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14186 / 0 / 616
Goodness of fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0372 R2= 0.1237
R indices (all data)	R1 = 0.0542 R2 = 0.1405
Largest diff. peak and hole	1.139 and -0.344 e. $Å^{-3}$

Table S2. Comparison of calculated and experimental structural parameters.

		Experimental Value	Calculated Value (**4**)
Distance (Å)	B1-Ni1	1.903(2)	1.90874
	O1-Ni1	1.978(1)	1.99717
	B2-O2	1.552(2)	1.55803
	O1-C25	1.219(2)	1.23942
	O2-C25	1.283(2)	1.27708
Angle (º)	B1-Ni1-O1	171.34(6)	167.393
	O1-C25-O2	124.1(1)	124.604
	C25-O2-B2	128.0(1)	123.263
	P1-Ni1-P2	158.61(2)	158.124
Dihedral angle (º)	Ni1-O1-C25-O2	-1.9(3)	2.757

Stoichiometric reaction with Et_3SiH and 4

In a glovebox, a solution of **4** (20 mg, 0.019 mmol) in C_6D_6 (0.3 mL) and a solution of Et_3SiH (3 μL, 0.019 mmol) in C_6D_6 (0.1 mL) were added to a J. Young valve NMR tube by means of microsyringes. Outside the glovebox, the NMR tube was charged with CO_2 (4 bar) and the temperature was gradually increased in the NMR spectrometer while the process was being monitored by ^{1}H NMR.

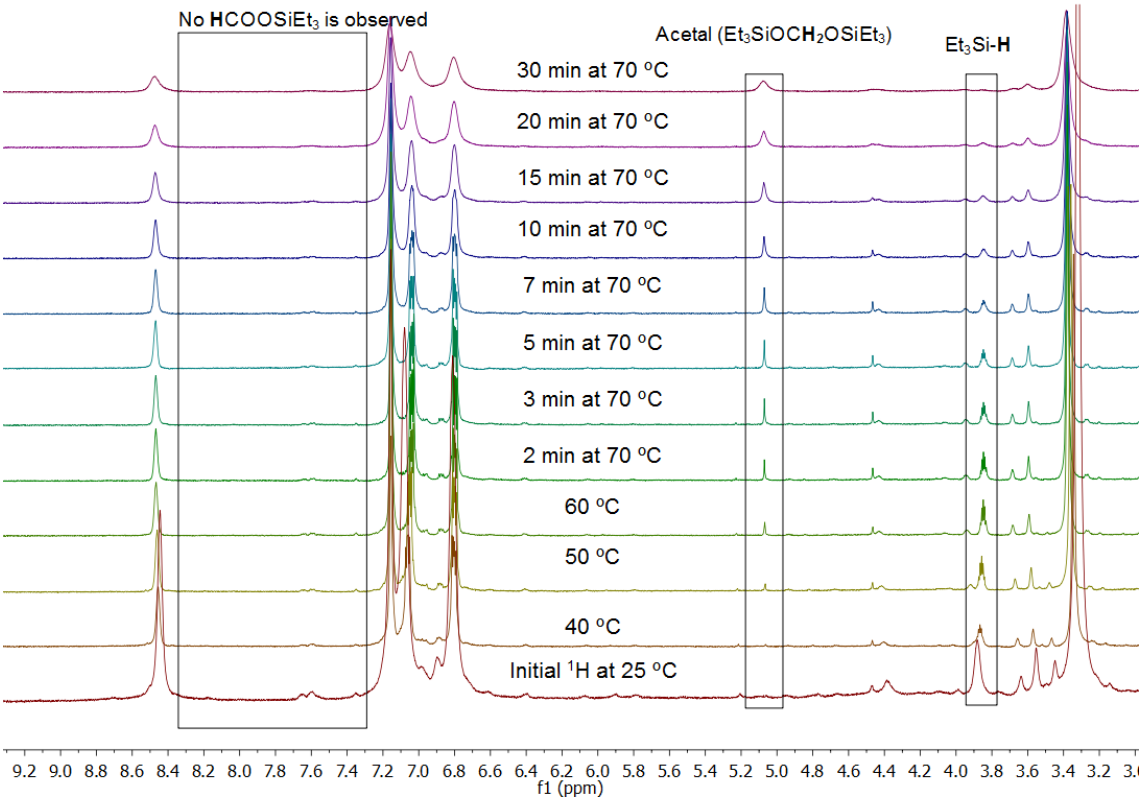


Figure S8.Monitoring of the reaction between Et_3SiH (1 eq) and CO_2 in the presence of **4** (1 eq).

Catalytic study with $^{13}CO_2$ and Et_3SiH

In a glovebox, a J. Young valve NMR tube was charged with Et_3SiH (304 μL, 1.91 mmol) and a solution of **4** (1 mg, 0.95 μmol) in C_6D_6 (100 μL) by means of microsyringes. Outside the glovebox, the NMR tube was charged with $^{13}CO_2$ (4 bar) and the reaction was monitored by ^{13}C NMR at 70 ºC. 8 hours later, $B(C_6F_5)_3$ (4 eq) was added to the NMR tube, which was heated up again at 70 ºC.

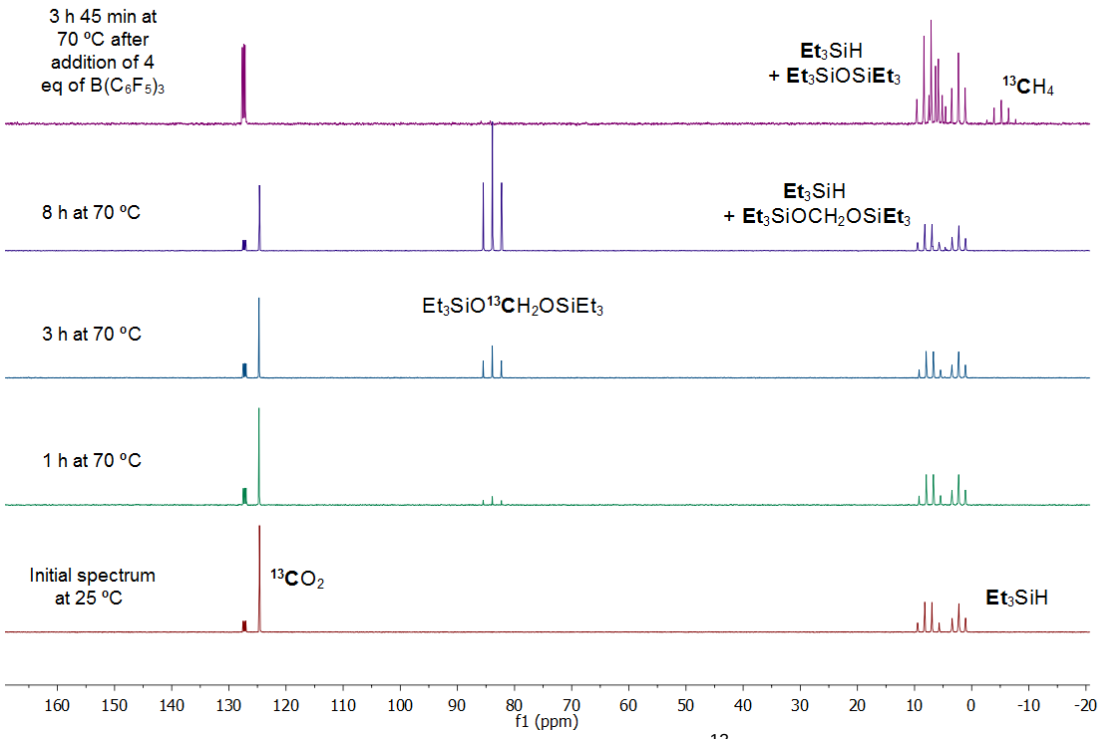


Figure S9. Monitoring of the reaction between Et_3SiH and $^{13}CO_2$ catalyzed by **4** (0.05% mol.). The intensity of the spectrum at the top was increased to get a better visualization.

Catalytic experiments

General procedure for a 0.05% molar catalyst loading

In a glovebox, a J. Young valve NMR tube was charged with a solution of **4** (1 mg, 0.95 μmol) in C_6D_6 (100 μL), after which silane (1.91 mmol) was added with a microsyringe. Outside the glovebox, CO_2 (4 bar) was charged and the tube was heated at 70 ºC in an oil bath. Conversion to bis(silyl)acetal was obtained from the integration values in the ^1H NMR spectra by using a relaxation delay (D1) of 10 seconds in the acquisition process.

Silane	Catalyst loading / % mol	[**4**]/mM	[Silane] /M	Total Volume / μL*	Conversion****	Bis(silyl) acetal	t / h	TON **	TOF / h^{-1}
Et_3SiH	0.05%	2.36	4.72	304 S + 100 B	60%	> 99%	21.5	1200	55.8
	0.1%	4.77	4.72	304 S + 100 B	91%	> 99%	34	910	26.8
	0.6%	10.9	1.81	101 S + 250 B	86%	> 99%	15.5	143	9.2
	1%	3	0.3	30 S + 600 B	90%	> 99%	70	90	1.3
Ph_2MeSiH	0.1%	3.98	4	378 S + 100 B	62%	> 99%	37.5	620	16.5
	0.1%	5	5.04	378 S (Neat)	41%	> 99%	22	410	18.6
	0.6%	10.9	1.81	126 S + 225 B	82%	> 99%	7.5	137	18.3
	1%	3	0.3	38 S + 600 B	90%	> 99%	45	90	2
Me_2PhSiH	0.6	10.9	1.83	97 S + 250 B	93%	78 % (8% Silyl methyl ether / 14% CH_4)***	3	121	40

Every catalytic experiment has been repeated at least 3 times. Partial decomposition of the catalyst was observed after the conversion values indicated above

*S = silane; B = d^6-Benzene

**TON = (μmoles of silane/μmoles of catalyst) * acetal ratio

*** Toluene was used as internal standard

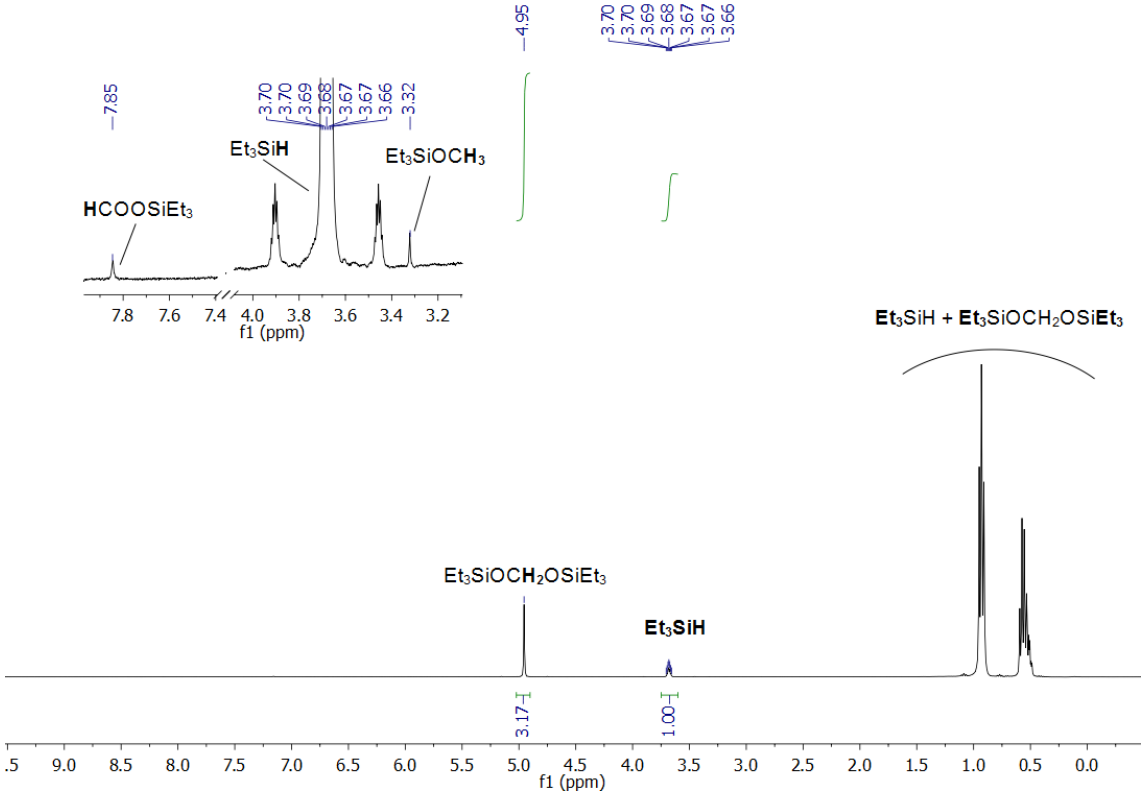


Figure S10. Representative example of catalysis with **4** (0.05% mol) and Et_3SiH after 21.5 h at 70 ºC. Inset: Enlargement of the spectrum, where some intermediates can be observed.

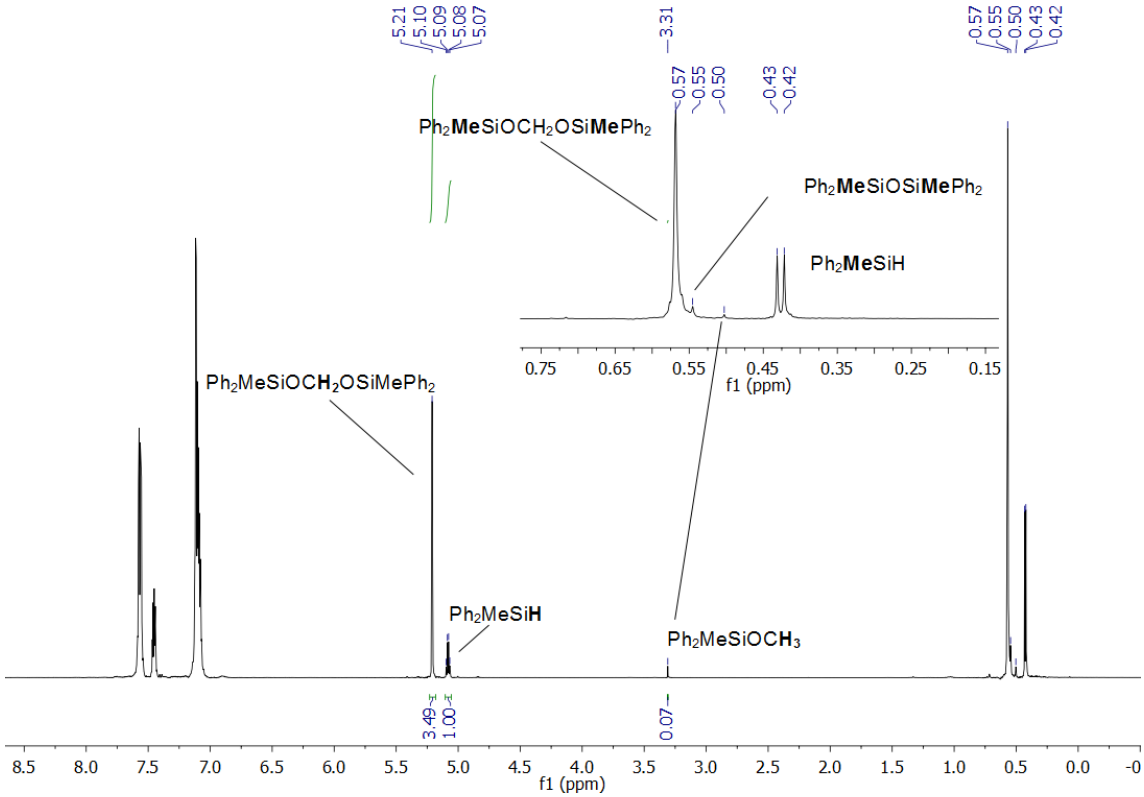


Figure S11. Representative example of catalysis with **4** (0.1% mol) and Ph_2MeSiH after 37.5 h at 70 ºC.

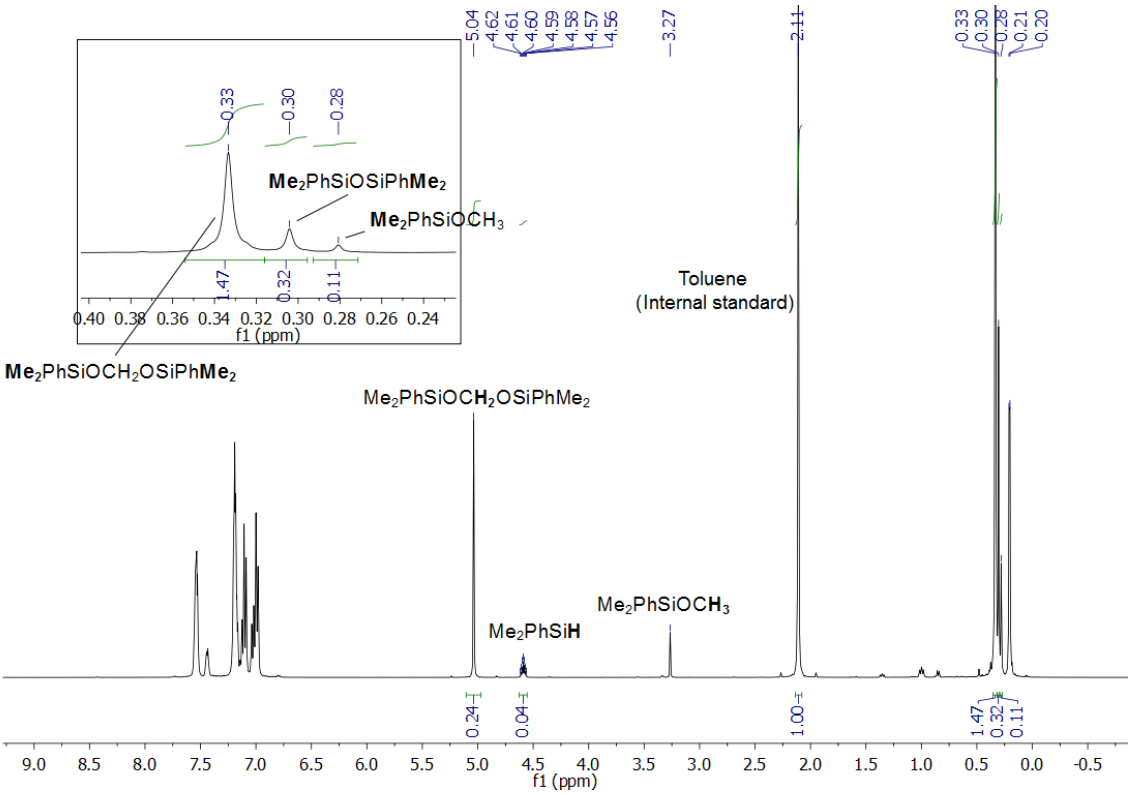


Figure S12. Representative example of catalysis with **4** (0.6% mol) and Me_2PhSiH after 3 h at 70 ºC. Toluene was added after the experiment as internal standard.

Isolation of acetal derived from Et_3SiH ($Et_3SiOCH_2OSiEt_3$)

The reaction mixture obtained after the catalysis was packed onto a silica column (ø = 1.2 cm, 40 g) in pentane, which was flushed with pentane to give 3,3,7,7-tetraethyl-3,7-disila-4,6-dioxanonane (R_f=0.64) as a colorless liquid after removing the solvent in vacuo.

^{1}H-NMR (400 MHz, C_6D_6, 25 ºC): δ 0.63 (q, 12 H, $^3J_{HH}$= 8 Hz, $CH_3C\boldsymbol{H}_2$), 1.01 (t, 18H, $^3J_{HH}$ = 8 Hz, $C\boldsymbol{H}_3CH_2$), 5.03 (s, 2 H, $OC\boldsymbol{H}_2O$) ppm. **^{13}C{^{1}H}-NMR** (100 MHz, C_6D_6, 25 ºC): δ 5.3 ($CH_3\boldsymbol{C}H_2$), 7.0 ($\boldsymbol{C}H_3CH_2$), 84.6 ($O\boldsymbol{C}H_2O$) **^{29}Si-NMR** (79 MHz, C_6D_6, 25 ºC): 18.3 (***Si***OCH_2O***Si***) ppm

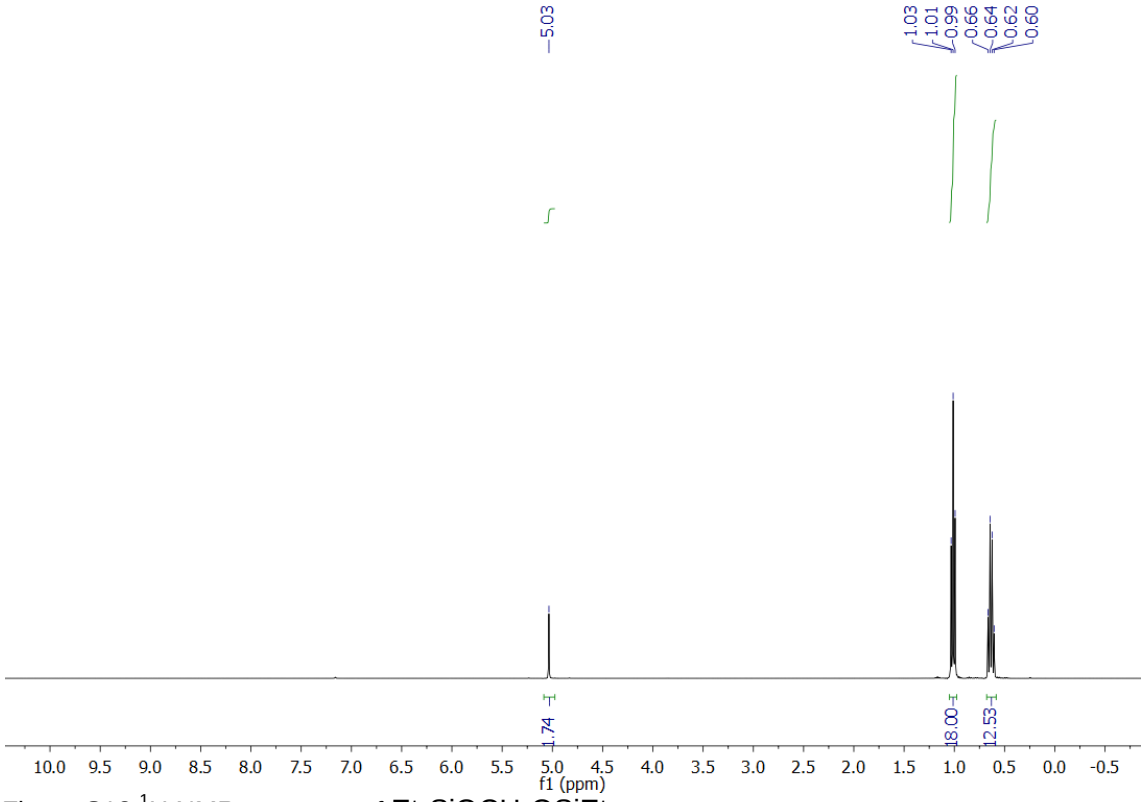


Figure S13.^{1}H NMR spectrum of $Et_3SiOCH_2OSiEt_3$

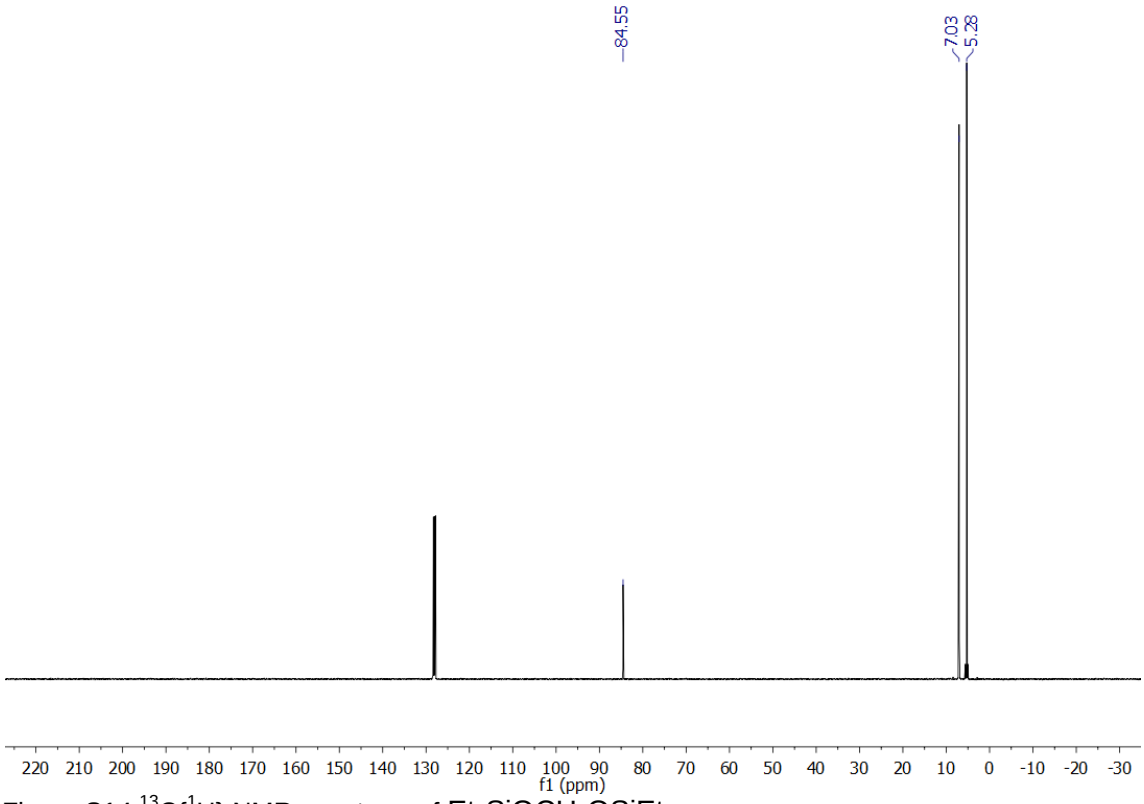


Figure S14.^{13}C{^{1}H} NMR spectrum of $Et_3SiOCH_2OSiEt_3$

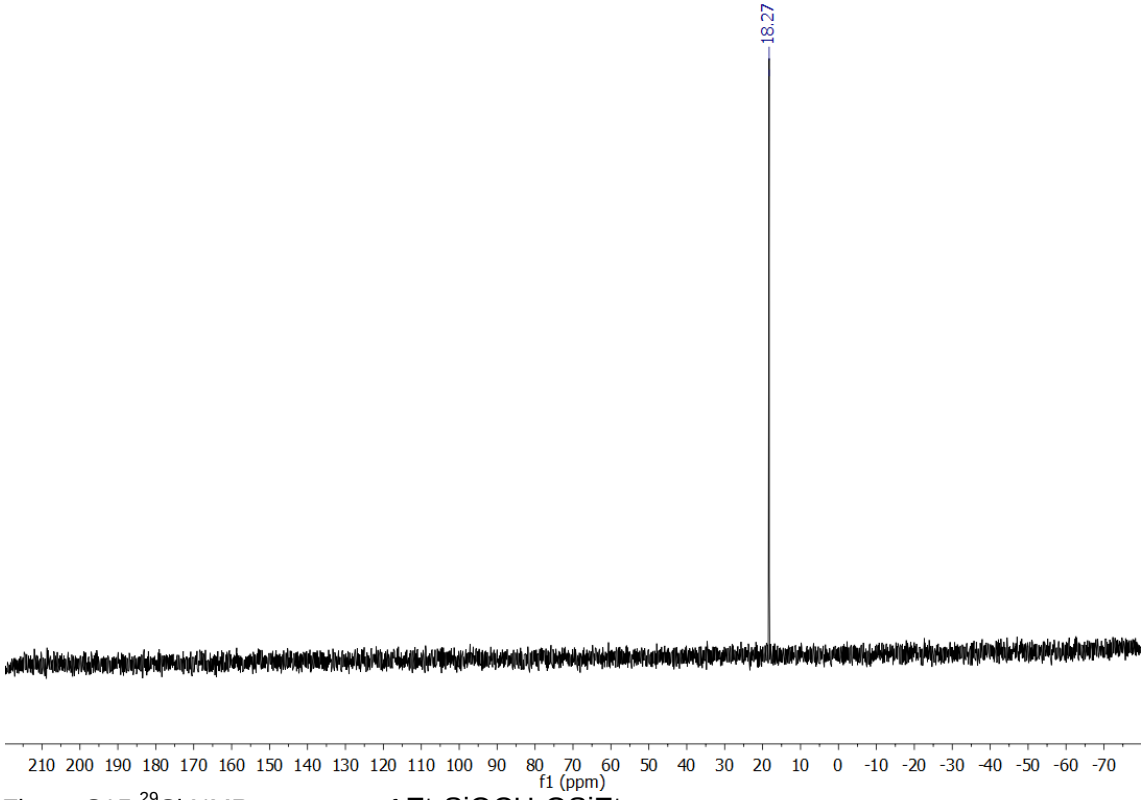
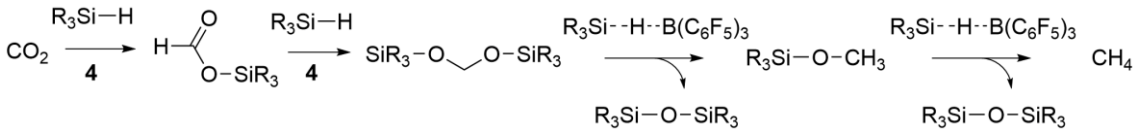


Figure S15.^{29}Si NMR spectrum of $Et_3SiOCH_2OSiEt_3$

Over-reduction by using Et_3SiH-$B(C_6F_5)_3$ complex



After isolating 3,3,7,7-tetraethyl-3,7-disila-4,6-dioxanonane, conversion to methane was achieved by adding $B(C_6F_5)_3$ (5 mg) and Et_3SiH (250 μL) to the NMR tube that contains it. The process was monitored by multinuclear NMR.

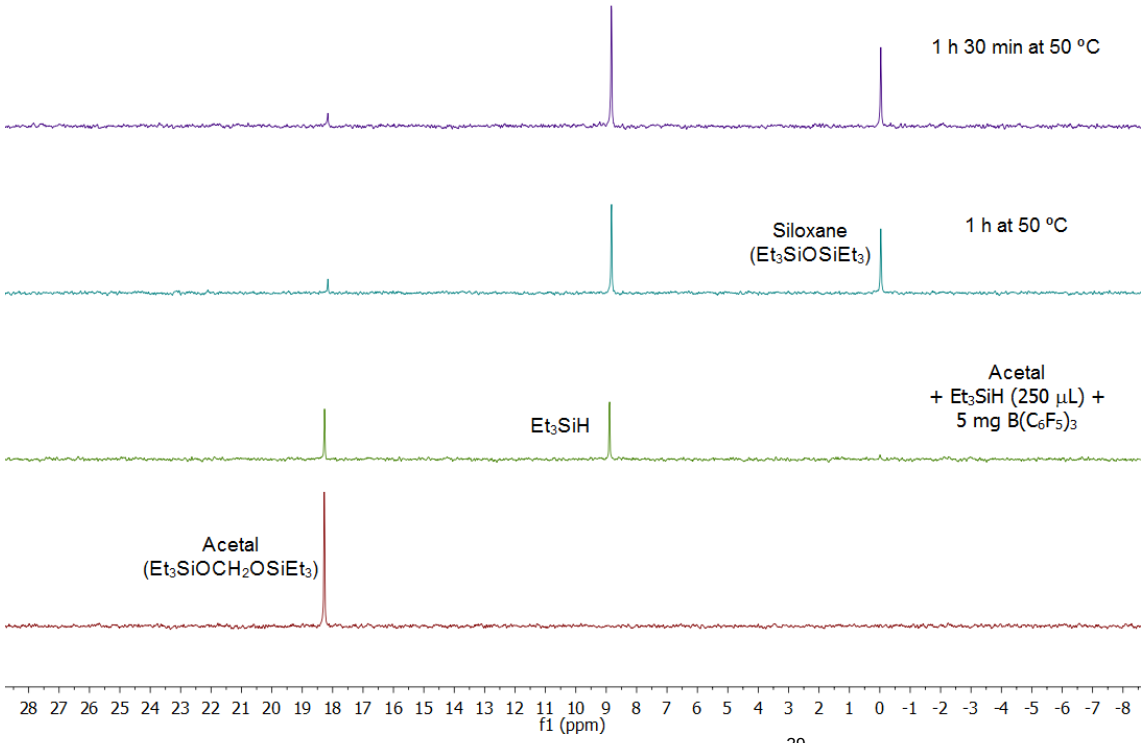


Figure S16. Monitoring of the over-reduction process through ^{29}Si NMR. No CH_3OSiEt_3 is observed, indicative of direct conversion to methane.

Exchange experiment with 4-$^{13}CO_2$ and $^{12}CO_2$ (1 bar)

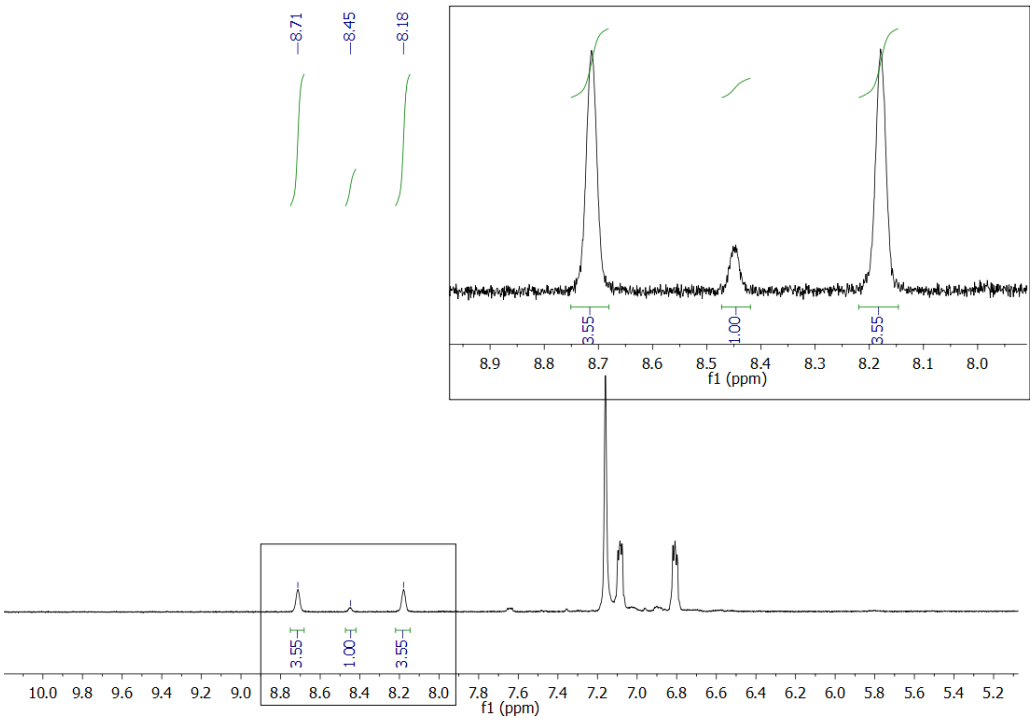


Figure S17. ^{1}H NMR spectrum of **4-$^{13}CO_2$** after 22 h heating at 70 ºC in the presence of $^{12}CO_2$ (1 bar).Incorporation of $^{12}CO_2$ in **4-$^{13}CO_2$** in a 12% ratio.

Computational details

Calculations were carried out at the DFT level with the Gaussian 09 suite of programs,[6] with the PBE0 functional.[7] The C, H, B, P, N, O and F atoms were represented by means of the 6-31g(d,p) basis set[8] whereas the Ni atom was described with the Stuttgart/Dresden Effective Core Potential and its associated basis set SDD.[9] Geometry optimizations were carried out in the gas phase without restrictions. Vibrational analysis was used to characterize the stationary points in the potential energy surface, as well as for calculating the Zero Point, Enthalpy and Gibbs energy corrections at 295 K and 1 atm. The effects of the bulk solvent (benzene) were accounted for in the final energy by single point calculations at the above level of theory with the SMD continuum model.[10]

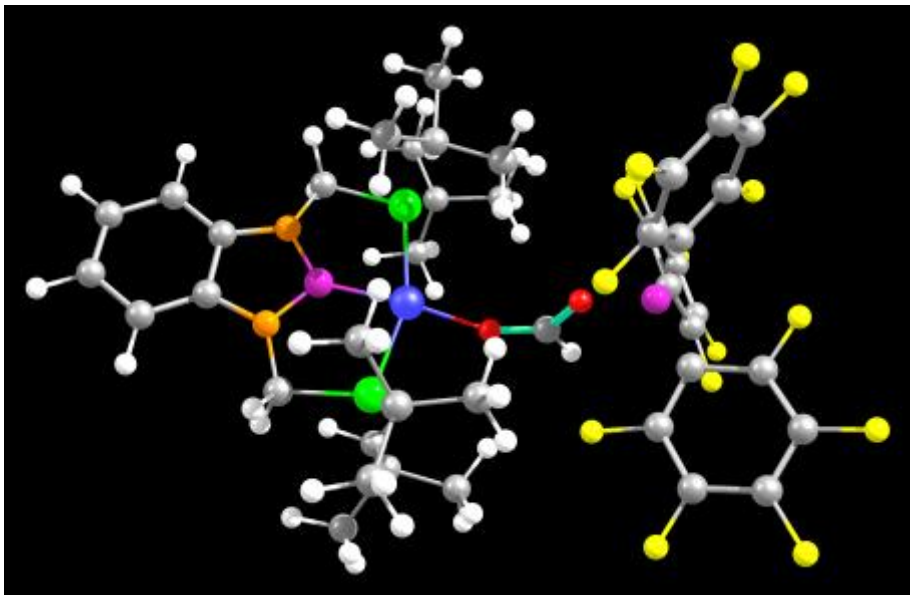


Figure S18. Calculated structure of **4**. Color code: C, grey; H, white; N, orange; B, pink; P, green; O, red; F, yellow; Ni, blue.

Tables of the optimized geometries (Cartesian coordinates, in Angstroms). Gas phase Energy (in Hartrees) in parenthesis.

CO_2
E = -188.38030341
G = -188.389157

C	0.000000000	0.000000000	0.000000000
O	0.000000000	0.000000000	1.165689000
O	0.000000000	0.000000000	-1.165689000

$B(C_6F_5)_3$
E = -2206.03800563
G = -2205.941937

B	0.000253000	-0.001358000	-0.001287000
C	1.424846000	-0.650204000	-0.001137000
C	2.499805000	-0.088222000	-0.699722000
C	1.706736000	-1.829695000	0.698065000
C	3.765721000	-0.654474000	-0.719141000
C	2.965385000	-2.411856000	0.718824000

C	3.998489000	-1.821076000	0.000284000
C	-0.149485000	1.556785000	-0.000769000
C	-1.173884000	2.207316000	-0.698656000
C	0.732306000	2.389888000	0.697618000
C	-1.315535000	3.586861000	-0.717813000
C	0.608225000	3.771127000	0.718324000
C	-0.420234000	4.371104000	0.000641000
C	-1.274640000	-0.909459000	-0.000413000
C	-1.327566000	-2.121680000	-0.698549000
C	-2.436359000	-0.561324000	0.698705000
C	-2.452744000	-2.932311000	-0.717945000
C	-3.571620000	-1.357653000	0.719376000
C	-3.578820000	-2.547849000	0.000937000
F	1.731451000	1.867749000	1.409118000
F	1.457624000	4.521532000	1.410326000
F	-0.546773000	5.687936000	0.001227000
F	-2.292428000	4.162204000	-1.409264000
F	-2.054912000	1.505254000	-1.411543000
F	2.331385000	1.025072000	-1.413259000
F	4.751687000	-0.095859000	-1.411551000
F	5.202609000	-2.368883000	0.001190000
F	3.191444000	-3.521918000	1.411752000
F	0.756270000	-2.434027000	1.411068000
F	-2.481882000	0.564202000	1.411542000
F	-4.645465000	-0.996051000	1.411932000
F	-4.656959000	-3.314372000	0.001236000
F	-2.464643000	-4.065452000	-1.410286000
F	-0.279966000	-2.534817000	-1.411859000

2 ([Ni]-H)

E = -1928.15549603

G = -1927.560782

Ni	0.000024000	-0.990589000	-0.116023000
B	-0.000005000	0.923971000	0.034280000
P	2.131608000	-0.629508000	-0.042634000
P	-2.131484000	-0.629448000	-0.042997000
N	1.141994000	1.798168000	0.024510000
N	-1.141988000	1.798173000	0.022988000
C	3.111882000	-1.305342000	-1.512645000
C	-2.455416000	1.239592000	-0.147791000
H	-2.877407000	1.495596000	-1.128655000
H	-3.171863000	1.576942000	0.613455000
C	0.697411000	5.506729000	-0.125108000
H	1.234155000	6.450059000	-0.165349000
C	2.455602000	1.239668000	-0.145239000
H	3.171164000	1.576250000	0.617183000
H	2.878746000	1.496657000	-1.125345000
C	0.713410000	3.115208000	-0.024564000
C	-2.885555000	-1.110417000	1.627410000
C	1.418187000	4.310748000	-0.075094000
H	2.504672000	4.314040000	-0.078548000

C	-1.418064000	4.310759000	-0.076887000
H	-2.504543000	4.314063000	-0.081735000
C	-0.713359000	3.115215000	-0.025476000
C	-3.111931000	-1.307138000	-1.512038000
C	-0.697215000	5.506734000	-0.125980000
H	-1.233901000	6.450068000	-0.166892000
H	-0.000133000	-2.526002000	-0.329940000
C	2.885560000	-1.112507000	1.627267000
C	-2.229309000	-0.194573000	2.671664000
H	-1.139436000	-0.284701000	2.648305000
H	-2.480465000	0.860787000	2.531370000
H	-2.575951000	-0.488901000	3.669856000
C	-2.488801000	-2.555534000	1.953739000
H	-1.407524000	-2.693636000	1.864143000
H	-2.795148000	-2.788426000	2.981309000
H	-2.967508000	-3.280035000	1.291047000
C	-4.405742000	-0.958566000	1.707717000
H	-4.922443000	-1.689700000	1.080032000
H	-4.730090000	-1.132625000	2.741502000
H	-4.745664000	0.042994000	1.423611000
C	-4.510216000	-0.712200000	-1.705129000
H	-4.949822000	-1.134339000	-2.617570000
H	-5.186233000	-0.944865000	-0.880183000
H	-4.491149000	0.374072000	-1.833561000
C	-3.205504000	-2.831906000	-1.409683000
H	-3.919039000	-3.146897000	-0.642175000
H	-3.557014000	-3.235844000	-2.367230000
H	-2.227934000	-3.271488000	-1.186809000
C	-2.243457000	-0.955330000	-2.729962000
H	-2.106740000	0.125619000	-2.845234000
H	-1.254725000	-1.417855000	-2.644094000
H	-2.726022000	-1.328769000	-3.641887000
C	2.227852000	-0.198914000	2.672538000
H	2.477705000	0.856962000	2.533812000
H	1.138098000	-0.290457000	2.648572000
H	2.574453000	-0.494214000	3.670460000
C	4.405584000	-0.959355000	1.708387000
H	4.729723000	-1.134659000	2.742029000
H	4.923135000	-1.689134000	1.079823000
H	4.744757000	0.042911000	1.425869000
C	2.490038000	-2.558483000	1.951231000
H	2.795745000	-2.792495000	2.978744000
H	1.408984000	-2.697557000	1.860516000
H	2.970119000	-3.281558000	1.287975000
C	4.510246000	-0.710435000	-1.705016000
H	5.186178000	-0.943954000	-0.880233000
H	4.949851000	-1.131771000	-2.617821000
H	4.491312000	0.375962000	-1.832446000
C	3.205249000	-2.830263000	-1.412321000
H	3.556318000	-3.232988000	-2.370539000
H	3.919080000	-3.146299000	-0.645519000
H	2.227725000	-3.270022000	-1.189606000

C	2.243391000	-0.951745000	-2.730021000
H	1.254630000	-1.414326000	-2.644781000
H	2.106691000	0.129366000	-2.843721000
H	2.725877000	-1.323904000	-3.642517000

3 ([Ni]-O_2CH)

E = -2116.58091929

G = -2115.969683

Ni	0.010189000	-0.772840000	0.086573000
B	0.046134000	1.125767000	-0.079105000
P	2.198219000	-0.405442000	0.079538000
P	-2.192346000	-0.335908000	0.009601000
N	1.188632000	1.991262000	0.036700000
N	-1.067964000	2.016917000	-0.234421000
C	2.974290000	-0.769473000	-1.606245000
C	3.157590000	-1.168933000	1.520174000
C	-2.395687000	1.497844000	-0.377097000
H	-2.777973000	1.629926000	-1.396304000
H	-3.110922000	1.972715000	0.307457000
C	0.803048000	5.705009000	-0.079890000
H	1.347317000	6.643209000	-0.026468000
C	2.485633000	1.440788000	0.302551000
H	2.818259000	1.653215000	1.326831000
H	3.259208000	1.816870000	-0.380083000
C	0.784958000	3.314274000	-0.036917000
C	-2.931147000	-0.499898000	1.746328000
C	1.502074000	4.501083000	0.035961000
H	2.578888000	4.492966000	0.179763000
C	-1.311408000	4.532321000	-0.334410000
H	-2.388067000	4.548124000	-0.478455000
C	-0.626811000	3.329764000	-0.217590000
C	-3.266409000	-1.139959000	-1.329124000
C	-0.579803000	5.720228000	-0.262814000
H	-1.098446000	6.670163000	-0.351984000
O	0.087505000	-2.654096000	0.622199000
C	-0.127044000	-3.601211000	-0.213766000
H	-0.063225000	-4.611957000	0.245585000
O	-0.381141000	-3.501212000	-1.414829000
C	-2.130713000	0.465560000	2.634838000
H	-1.064191000	0.217531000	2.629461000
H	-2.234385000	1.512105000	2.332211000
H	-2.494702000	0.379300000	3.666066000
C	-4.420455000	-0.162684000	1.841191000
H	-5.040105000	-0.900055000	1.324009000
H	-4.720741000	-0.170320000	2.896360000
H	-4.659563000	0.829022000	1.443326000
C	-2.690498000	-1.924670000	2.262628000
H	-3.301584000	-2.663508000	1.739097000
H	-1.643533000	-2.222233000	2.155607000
H	-2.962354000	-1.965221000	3.324970000
C	-3.573633000	-2.602378000	-0.996558000

H	-4.259854000	-2.698102000	-0.149995000
H	-4.064470000	-3.058404000	-1.865153000
H	-2.663701000	-3.173298000	-0.803591000
C	-2.394359000	-1.096059000	-2.594189000
H	-1.497848000	-1.710017000	-2.463827000
H	-2.969350000	-1.498895000	-3.437393000
H	-2.098209000	-0.073779000	-2.857828000
C	-4.587048000	-0.405051000	-1.593839000
H	-5.114693000	-0.929543000	-2.399879000
H	-5.249399000	-0.392412000	-0.725736000
H	-4.443173000	0.625889000	-1.928459000
C	2.241707000	-0.967694000	2.738196000
H	2.006743000	0.088373000	2.914479000
H	1.304352000	-1.517128000	2.611016000
H	2.747510000	-1.346539000	3.635115000
C	4.516033000	-0.513437000	1.793718000
H	4.432348000	0.551472000	2.028982000
H	4.967624000	-0.999242000	2.667641000
H	5.214535000	-0.624378000	0.961880000
C	3.349574000	-2.673220000	1.303943000
H	2.401120000	-3.160734000	1.064750000
H	4.075901000	-2.885269000	0.513990000
H	3.737104000	-3.115641000	2.230142000
C	4.490190000	-0.563990000	-1.646414000
H	5.018056000	-1.313048000	-1.049906000
H	4.835251000	-0.672585000	-2.681941000
H	4.794988000	0.430540000	-1.303642000
C	2.631930000	-2.203056000	-2.029672000
H	3.116370000	-2.951726000	-1.398739000
H	1.554669000	-2.395110000	-2.012251000
H	2.990094000	-2.358625000	-3.055059000
C	2.300795000	0.186310000	-2.603339000
H	2.505922000	1.240657000	-2.395129000
H	2.682096000	-0.033848000	-3.607726000
H	1.215623000	0.046860000	-2.615676000

4 ([Ni]-$O_2CH \cdot B(C_6F_5)_3$)

E = -4322.66826514

G = -4321.934800

Ni	2.450248000	0.083018000	-0.461176000
B	4.299060000	-0.056875000	-0.007741000
P	3.027712000	2.260011000	-0.406569000
P	2.631298000	-2.134263000	-0.124539000
N	5.259409000	1.004810000	0.092525000
N	5.063229000	-1.258152000	0.173090000
C	2.380734000	3.122758000	1.145472000
C	2.731362000	3.233006000	-2.003022000
C	4.459136000	-2.541315000	-0.027077000
H	4.670084000	-3.250651000	0.783407000
H	4.793134000	-3.002895000	-0.964767000
C	8.882603000	0.268356000	0.618788000

H	9.861515000	0.725434000	0.727006000
C	4.892065000	2.355316000	-0.213567000
H	5.353816000	2.693890000	-1.149295000
H	5.177605000	3.068936000	0.570127000
C	6.524365000	0.473668000	0.295069000
C	2.035844000	-3.260320000	-1.525743000
C	7.764664000	1.083331000	0.430477000
H	7.863067000	2.164337000	0.388651000
C	7.519780000	-1.743078000	0.530468000
H	7.430999000	-2.825197000	0.563872000
C	6.401828000	-0.940424000	0.345002000
C	1.978213000	-2.643949000	1.575766000
C	8.762131000	-1.121032000	0.668175000
H	9.648566000	-1.730824000	0.814023000
O	0.665765000	0.219243000	-1.347598000
C	-0.567750000	0.197132000	-1.228746000
H	-1.176409000	0.278947000	-2.140743000
O	-1.187311000	0.070362000	-0.119240000
B	-2.740273000	0.008690000	-0.009856000
C	-2.984468000	-0.556386000	1.508496000
C	-3.246952000	-0.984342000	-1.212402000
C	-3.396272000	1.507347000	-0.080983000
C	-3.910183000	-1.531326000	1.873698000
C	-2.273972000	-0.004396000	2.573587000
C	-3.958296000	-0.591652000	-2.345154000
C	-2.882576000	-2.330854000	-1.202353000
C	-4.737525000	1.672549000	0.266987000
C	-2.748576000	2.684664000	-0.427407000
C	-4.091983000	-1.964094000	3.182995000
F	-4.691676000	-2.115091000	0.959059000
C	-2.417776000	-0.411205000	3.894558000
F	-1.389635000	0.984118000	2.363316000
C	-4.289076000	-1.460205000	-3.383821000
F	-4.349597000	0.676296000	-2.518242000
C	-3.171675000	-3.226022000	-2.220567000
F	-2.194985000	-2.830587000	-0.162143000
C	-5.380673000	2.901858000	0.308985000
F	-5.481481000	0.599893000	0.564716000
C	-3.344502000	3.940399000	-0.393682000
F	-1.464904000	2.674428000	-0.845455000
C	-3.337408000	-1.402884000	4.202825000
F	-4.986160000	-2.910767000	3.466036000
F	-1.689855000	0.149023000	4.862738000
C	-3.889716000	-2.786071000	-3.324995000
F	-4.966421000	-1.018795000	-4.441874000
F	-2.755441000	-4.491680000	-2.154449000
C	-4.673902000	4.052068000	-0.019337000
F	-6.663724000	2.989683000	0.653655000
F	-2.646643000	5.028162000	-0.726937000
F	-3.496323000	-1.807116000	5.460397000
F	-4.178967000	-3.623068000	-4.315850000
F	-5.267729000	5.241322000	0.016700000

C	0.865886000	2.924923000	1.236809000
H	0.584773000	1.870749000	1.176854000
H	0.515718000	3.302933000	2.204609000
H	0.320483000	3.458361000	0.458192000
C	3.026665000	2.397476000	2.335501000
H	2.783714000	1.331032000	2.328912000
H	4.115667000	2.497786000	2.365366000
H	2.627775000	2.825401000	3.262414000
C	2.715470000	4.614326000	1.214777000
H	2.167017000	5.191489000	0.465652000
H	2.416655000	4.996706000	2.198172000
H	3.785095000	4.817968000	1.097645000
C	1.244997000	3.552006000	-2.171262000
H	0.895871000	4.300627000	-1.455513000
H	1.083065000	3.961417000	-3.175740000
H	0.625320000	2.660572000	-2.069211000
C	3.158875000	2.272173000	-3.124148000
H	2.543564000	1.367267000	-3.124585000
H	3.034015000	2.772287000	-4.092258000
H	4.209588000	1.972169000	-3.042506000
C	3.542704000	4.528964000	-2.111650000
H	3.327973000	4.990547000	-3.083123000
H	3.280580000	5.256309000	-1.341418000
H	4.622602000	4.361781000	-2.071243000
C	0.559293000	-2.092471000	1.749587000
H	0.204891000	-2.343115000	2.756854000
H	0.527470000	-1.004278000	1.646467000
H	-0.154961000	-2.508305000	1.038128000
C	2.880328000	-1.971853000	2.621144000
H	3.904227000	-2.356848000	2.618380000
H	2.925885000	-0.888851000	2.478269000
H	2.458403000	-2.162326000	3.614850000
C	1.983798000	-4.155972000	1.812108000
H	1.693250000	-4.349461000	2.851602000
H	1.264631000	-4.676774000	1.175004000
H	2.972211000	-4.603203000	1.662075000
C	0.511115000	-3.366378000	-1.519074000
H	0.180966000	-3.878896000	-2.430465000
H	0.131389000	-3.941226000	-0.671960000
H	0.039004000	-2.383078000	-1.500609000
C	2.639701000	-4.669587000	-1.497850000
H	2.366163000	-5.229246000	-0.601914000
H	2.255038000	-5.226429000	-2.360847000
H	3.730033000	-4.666232000	-1.581647000
C	2.479021000	-2.548491000	-2.813751000
H	1.998745000	-1.570361000	-2.911557000
H	3.564122000	-2.402544000	-2.859236000
H	2.192647000	-3.159912000	-3.678056000

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7. This functional has been shown to reproduce the uniform electron gas limit (UEG) and being effective in describing metal hydride, dihydrogen and hydrogen bond situations; Pantazis, D.A.; McGrady, J.E.; Maseras, F.; Etienne, M. *J. Chem. Theor. Comput.* **2007**, 3, 1329-1336. In this case calculations with the B3LYP functional gave higher relative energies for both transition states.

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