Supporting information

Hydrazine N-N Bond Cleavage over Silica-Supported Tantalum Hydrides

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TABLE OF CONTENTS

Experimental Details

All experiments were carried out by using standard air-free methodology in an argon-filled Vacuum Atmospheres glovebox, on a Schlenk line or in a Schlenk-type apparatus interfaced to a high-vacuum line (10^{-5} Torr). $[Ta(CH_2C(CH_3)_3)_3(=CHC(CH_3)_3)]$ was commercial from STREM company without further purification. MCM-41 mesoporous silica was purchased from Sigma-Aldrich Company. MCM-41 supported tantalum hydrides $[(\equiv SiO)_2TaH]$, **1a**, and $[(\equiv SiO)_2TaH_3]$, **1b**, were prepared by impregnation in pentane or by sublimation for *in situ* IR monitoring as previously reported by the reaction of $[Ta(CH_2{}^tBu)_3(=CH{}^tBu)]$ with MCM-41 previously dehydroxylated at 500°C, followed by hydrogenolysis (550 Torr, 15h, 150°C).[1] Dry pentane was distilled on NaK alloy followed by degassing through three freeze-pump-thaw cycles.

Gas-phase analysis of alkanes and H_2: Gas phase analysis was performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and an Al_2O_3/KCl on fused silica column (50m X 0.32 mm). Dihydrogen gas phase analysis was performed on an intersmat-IGC 120-MB gas chromatograph equipped with a catharometer (TCD, thermal conductivity detector).

Infrared spectra were recorded on a Nicolet 550-FT spectrometer by using an infrared cell equipped with CaF_2 windows, allowing *in situ* monitoring under controlled atmosphere. Typically 36 scans were accumulated for each spectrum (resolution, 4 cm^{-1}). DRIFT spectra were recorded on a Nicolet 550-FT spectrometer and sample loading was performed in argon-filled glovebox.

Solid-state NMR spectra were recorded on a Brüker DSX-500 spectrometer equipped with a standard 4-mm double-bearing probe head and operating at 75.47, 500, MHz for ^{13}C, ^{1}H and ^{15}N respectively.

The samples were introduced in the rotor made of zirconia in a glovebox and tightly closed. Compressed air was used for both of bearing and driving the rotors.

Preparation of $[(\equiv SiO)_2TaH]$ and $[(\equiv SiO)_2TaH_3]$, 1:

Powder of $[(\equiv SiO)_2Ta(=CH{}^tBu)(CH_2{}^tBu)_2]$ (500mg, 0.32 mmol Ta) was twice treated at 150°C with anhydrous hydrogen (600 torr, 16.4 mmol, 65 equivalent / Ta) for 15 h. Gas chromatography analysis indicated the formation of 13±2 CH_4 coming from the hydrogenolysis of 2,2-dimethylpropane, CMe_4 (2.6±0.4 CMe_4/Ta, expected 3). The gas

evolved during the reaction was removed under vacuum and the final hydrides [(≡SiO)$_2$TaH], **1a**, and [(≡SiO)$_2$TaH$_3$], **1b**, were obtained as a brown powder. As already reported, some surface alkyl groups (<0.1 C/Ta) resist hydrogenolysis. Elemental Analysis: Ta 15.91%wt C 0.67%wt. Solid state ^{1}H MAS NMR = 29.5, 26.8, 23.2, 18.0, 13.0 (Ta(***H***)$_x$), 4.3, 4.0 (Si***H*** and Si***H$_2$***), 1.8 (SiO***H***), 0.8 (C***H$_n$***) ppm. IR: 3747 (ν $_{OH}$), 3270-2850 (ν $_{CH}$), 2270 (ν $_{SiH}$), 2220 (ν $_{SiH2}$), 2100-1600 (δ $_{Si-O-Si}$), 1890-1700 (ν $_{TaH}$), 1467 w, 1362 (δ $_{CH}$) cm^{-1}.

In-situ IR study of the reaction of [(≡SiO)$_2$TaH$_x$], 1 with hydrazine:

Hydrazine was prepared by the reaction of KOH with hydrazine monohydrate 64-65 %, reagent grade, 98 % (Sigma Aldrich) according to literature procedure.[2] Addition of N_2H_4 (14.4 torr at 25 °C) on [(≡SiO)$_2$TaH$_x$], **1**, (25 mg, 0.025 mmol Ta) was done at room temperature and gave the following IR peaks.

Selected IR frequencies for the reaction of physisorbed N_2H_4: 3368 (ν $_{NH}$), 3290 (ν $_{NH}$), 3197 (ν $_{NH}$), 1612 (δ $_{NH2}$) cm^{-1}.

Selected IR frequencies for the reaction of [(≡SiO)$_2$TaH$_x$)] with N_2H_4: 3747 (ν $_{OH}$), 3359 (ν $_{NH}$), 3285 (ν $_{NH}$), 3190 (ν $_{NH}$), 3270-2850 (ν $_{CH}$), 2270 (ν $_{SiH}$), 2220 (ν $_{SiH2}$), 2100-1600 (δ $_{Si-O-Si}$), 1890-1700 (ν $_{TaH}$),1605 (δ $_{NH2}$) cm^{-1}.

Excess of the hydrazine was needed to consume the total TaH peaks and new peaks in NH region appeared with thermal-treatment at 100 °C.

Selected IR frequencies for the reaction of [(≡SiO)$_2$TaH$_x$)] with N_2H_4 at 100 °C: 3747 (ν $_{OH}$), 3494 (ν $_{NH}$), 3358 (ν $_{NH}$), 3374 (ν $_{NH}$), 3294 (ν $_{NH}$), 3270-2850 (ν $_{CH}$), 2270 (ν $_{SiH}$), 2220 (ν $_{SiH2}$), 2100-1600 (δ $_{Si-O-Si}$),1613 (δ $_{NH2}$) cm^{-1}.

The same experiment was also done with [(≡SiO)$_2$TaH$_x$], **1**, (15 mg, 0.02 mmol) with N_2H_4 which didn't lead to the complete consumption of TaH peaks at room temperature.

Selected IR frequencies for the reaction with N_2H_4 at 150 °C: 3747 (ν $_{OH}$), 3500 (ν $_{TaN-H}$), 3461 (ν $_{N-H}$), 3372 (ν $_{TaN-H}$), 3270-2850 (ν $_{CH}$), 2270 (ν $_{SiH}$), 2220 (ν $_{SiH2}$), 2100-1600 (δ $_{Si-O-Si}$), 1890-1700 (ν $_{TaH}$), 1520 (δ $_{TaNH2}$) cm^{-1}.

Elemental analysis: Ta 15,7 %$_{wt}$; N 1,34 %$_{wt}$. (N/Ta by e.a.= *ca*.0.96 and 0.95).

The reaction of [(≡SiO)$_2$TaH$_x$], 1 with ^{15}N-labeled hydrazine:

A disk of [(≡SiO)$_2$TaH$_x$], **1**, (25 mg, 0.025 mmol Ta), prepared as previously reported, was treated by $^{15}N_2H_4$ (14.4 torr at 25 ° C). Peaks in the ν (NH) and δ (NH$_2$) region confirmed the presence of ^{15}N-hydrazine on the pellet with an expected redshift.

Selected IR frequencies for the reaction with $^{15}N_2H_4$ (ν (NH): 3348, 3278, 3189 cm^{-1}; δ (NH$_2$): 1608 cm^{-1}).

Heating the sample at 100 °C for 2 h gave the peaks at 1516 and 1545 cm^{-1} leading the Ta-^{15}NH$_2$ and Si-^{15}NH$_2$ respectively.

Control experiment on hydrazine stability at 100°C

To eliminate the possibility that the reaction can occur in the absence of the metal-hydride, a control experiment was carried out. Hydrazine was heated at 100 °C on tantalum-free starting silica pellet. The IR spectrum show bands at 3367, 3291, 3198 and 1612 cm$^{-1,}$ mentioned above, which are characterized of stretching ν(NH)$_x$ and δ(NH$_2$) modes of physisorbed hydrazine on pure silica (Figure S1). Physisorbed hydrazine cannot be substantially removed under dynamic vacuum treatment (1h at 10^{-5} torr). The evolution of the IR spectrum with temperature shows that hydrazine starts decomposing above 150 °C, when bands at 3408 and 3322 cm^{-1} start to appear (see spectrum Figure S2d). These bands were previously assigned to the stretching frequencies of ammonia physisorbed on pure silica (Figure S2e).[1] This control experiment indicates that hydrazine does not transform at 100 °C in the absence of tantalum complexes.

Table S1. Relative energies (kcal/mol) with respect to **Ib** + N_2H_4 of products and potential reaction intermediates as function of the level of theory, basis sets and silica surface modeling (cluster *vs.* periodic). See Figure S6 for periodic model representation and Figures S6 to S9 for species labeling.

Species	M06/ aug-cc-pVDZ	PBE-D3/ aug-cc-pVDZ	PBE-D3/ DZVP	Periodic
Ia	40.0	45.4	45.2	46.1
Ib	0.0	0.0	0.0	0.0
Ib-N_2H_4-mer	-29.9	-29.5	-29.1	-37.4
Ib-N_2H_4-fac	-25.6	-23.9	-24.2	-28.6
Ib-η^1-N_2H_4	-24.8	-24.1	-25.4	-27.3
II	-76.3	-71.9	-81.3	-82.0
III	-87.6	-82.6	-89.2	-91.7
IV-eq	-31.6	-29.5	-33.4	-34.7
IV-cis	-30.4	-28.0	-31.9	-33.0
V-Is1	-88.6	-85.0	-88.9	-91.4
V-Is2	-86.2	-81.9	-86.4	-94.5

Table S2. Differences in the relative energies (in kcal/mol) with respect to **Ib** + N_2H_4 of products and intermediates as function of: a) level of theory, b) basis sets and c) surface modeling. See Figure S6 for periodic model representation and Figures S7 to S9 for species labeling.

Species	$\Delta E_{functional}$[a]	ΔE_{basis}[b]	ΔE_{model}[c]
Ia	-5.4	-0.2	+0.9
Ib	--	--	--
Ib-N_2H_4-mer	-0.4	+0.4	-8.3
Ib-N_2H_4-fac	-1.7	-0.3	-4.4
Ib-η^1-N_2H_4	-0.7	-1.3	-1.9
II	-4.4	-9.3	-0.7
III	-5.0	-6.6	-2.5
IV-eq	-2.1	-3.9	-1.3
IV-cis	-2.4	-3.9	-1.1
V-Is1	-3.6	-3.9	-2.5
V-Is2	-4.3	-4.5	-8.1

[a] Energy difference between the M06/aug-cc-pDVZ and PBE-D3/aug-cc-pDVZ calculations. A positive value indicates that M06 predicts a more stable intermediate with respect to **Ib** + N_2H_4 reactants asymptote.

[b] Energy difference between the PBE-D3/aug-cc-pDVZ and PBE-D3/DZVP calculations. A positive value indicates that aug-cc-pDVZ predicts a more stable intermediate with respect to **Ib** + N_2H_4 reactants asymptote.

[c] Energy difference between the cluster and the periodic models using the same PBE-D3/DZVP methodology. A positive value indicates that the cluster model predicts a more stable intermediate with respect to **Ib** + N_2H_4 reactants asymptote.

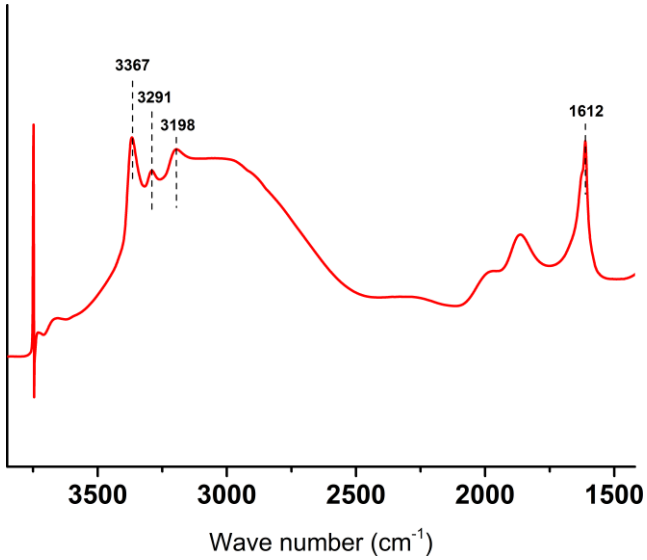


Figure S1. Infrared spectrum after hydrazine addition on MCM-41 pellet at room temperature.

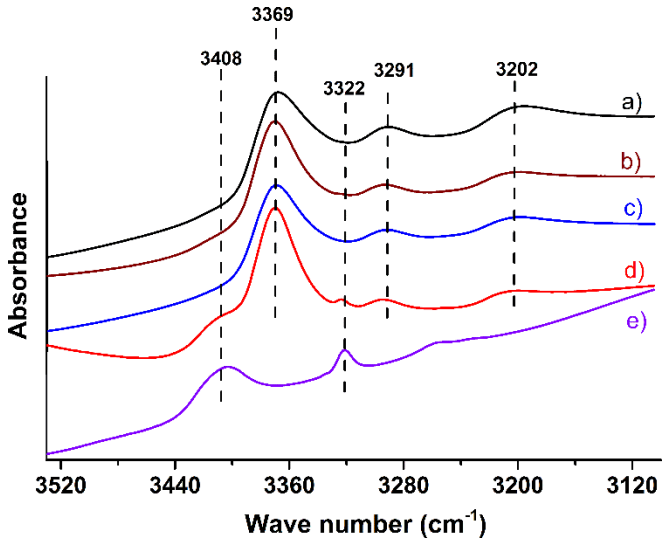


Figure S2. The evolution of the IR spectra between 3520 and 3120 cm^{-1} of a MCM-41 pellet (ca. 25 mg, pretreated under vacuum at 500°C for 15 h) either in the presence of hydrazine (a) at room temperature (b) after 1h at 50°C (c) after 1h at 100°C (d) after 1h at 150°C or (e) in the presence of ammonia at room temperature.

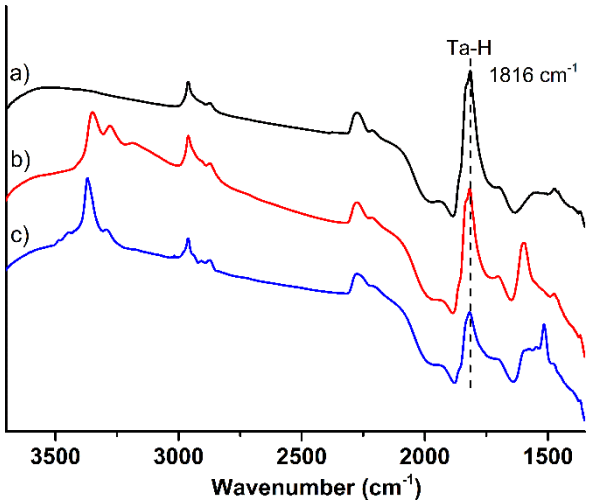
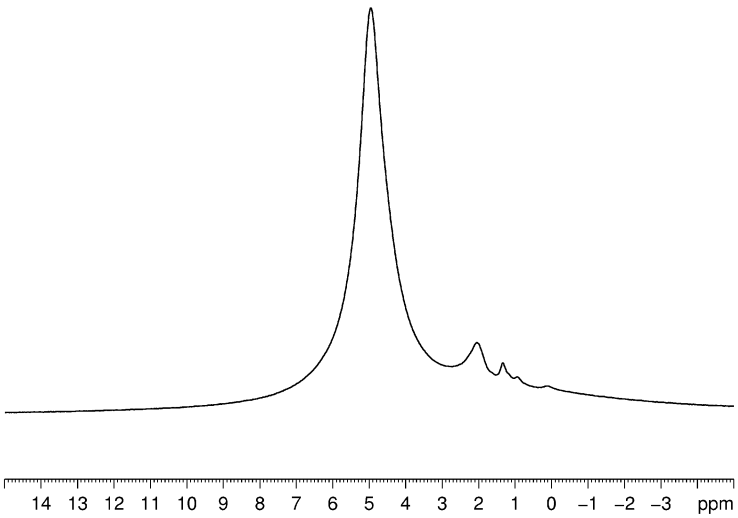


Figure S3. Difference IR spectra for (a) starting tantalum hydrides [$(\equiv SiO)_2TaH_x$ x: 1, 3] (b) after addition of $^{15}N_2H_4$ for 1h at RT (followed by gas-phase evacuation) (c) after 2h at 100°C. Spectrum of Starting unfunctionalized MCM-41 silica subtracted in all cases (ca. 25 mg, pretreated under vacuum at 500°C for 15 h). Original spectra before subtraction are reported in Figure 2 of the manuscript.



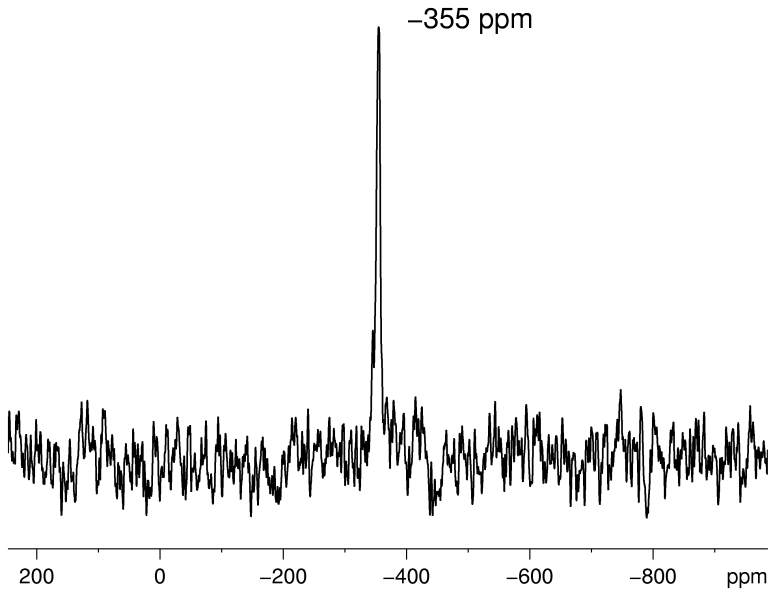


Figure S4. MAS SS ^{1}H-NMR (above) and CP ^{15}N NMR (below) spectra of N_2H_4 physisorbed on silica pellet (MCM-41 previously dehydroxylated at 500 °C).

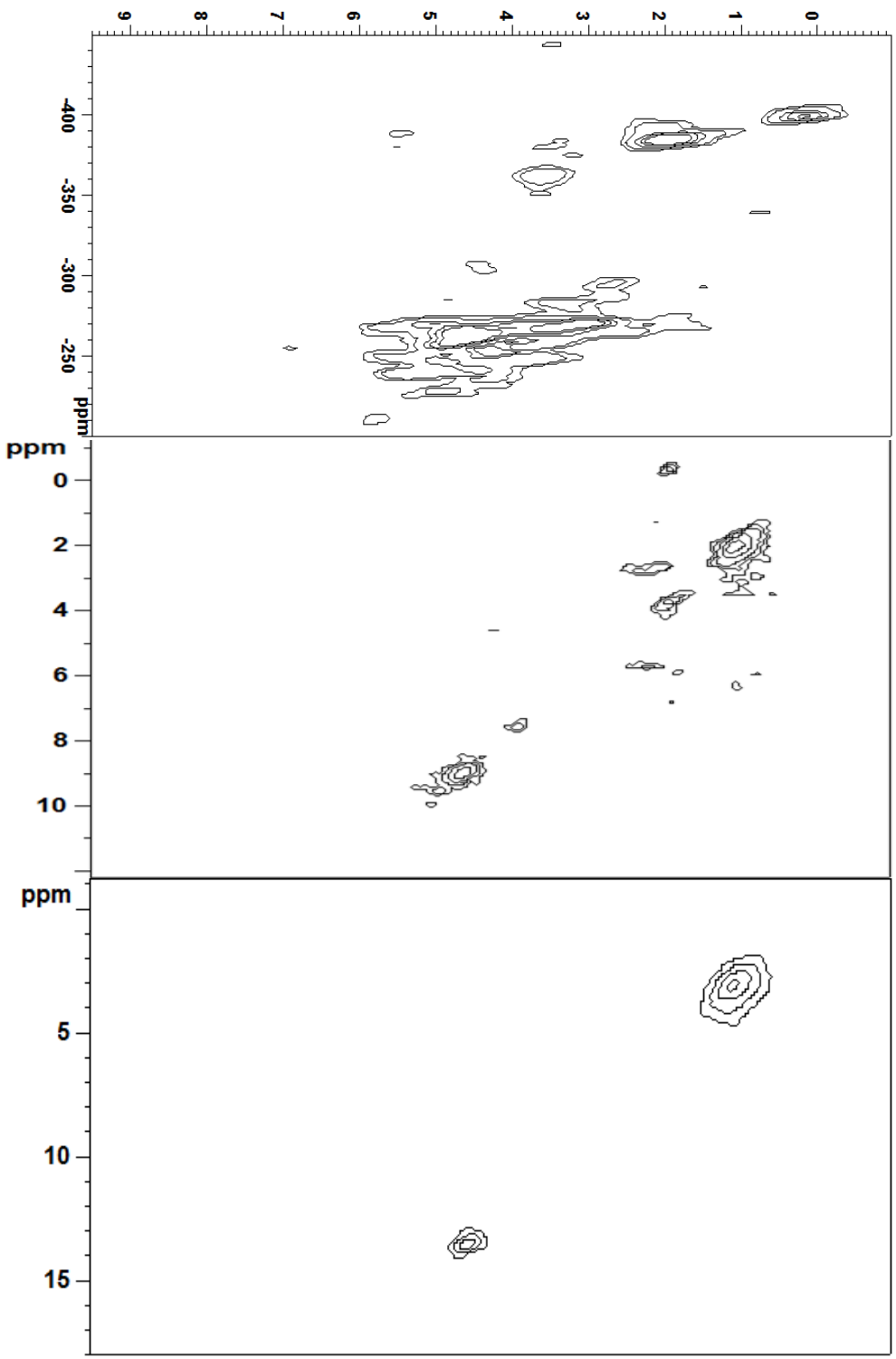


Figure S5: Enlarged Two-dimensional solid-state MAS correlation spectra reported in Figure 4 of manuscript.

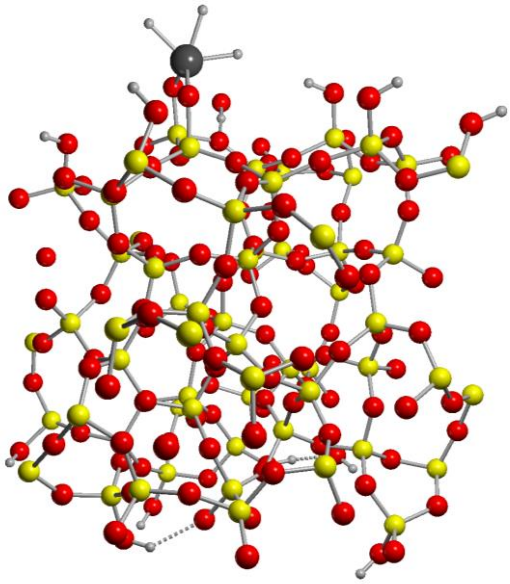


Figure S6. Unit cell of Periodic model

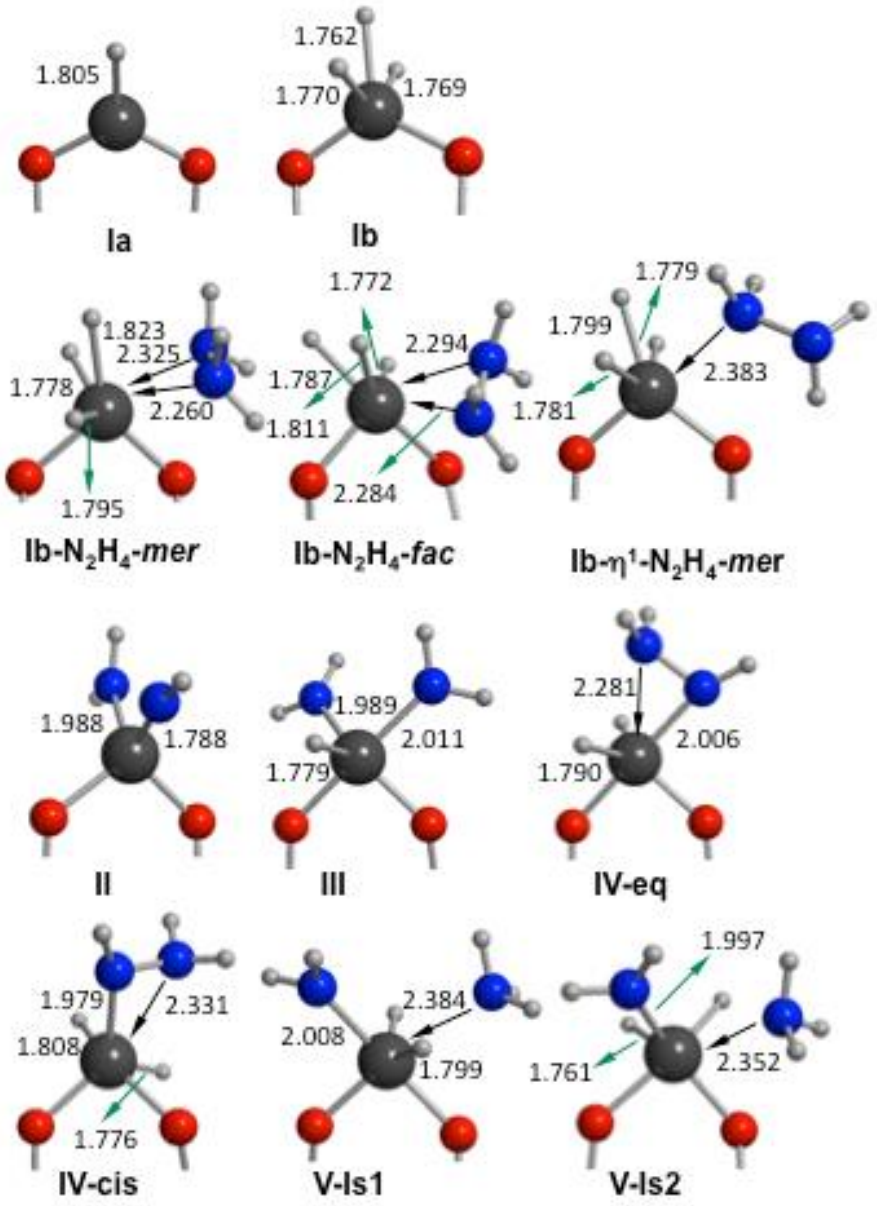


Figure S7. Structures and selected distances in Å for all intermediates involved in the reaction of N_2H_4 with **1b**. Geometries were obtained with the cluster model of the silica surface, the PBE-D level of theory and the basis sets, we used for the Gaussian09 calculations (see computational details section). Black arrows are used for formal donor – acceptor interactions and green arrows for distances.

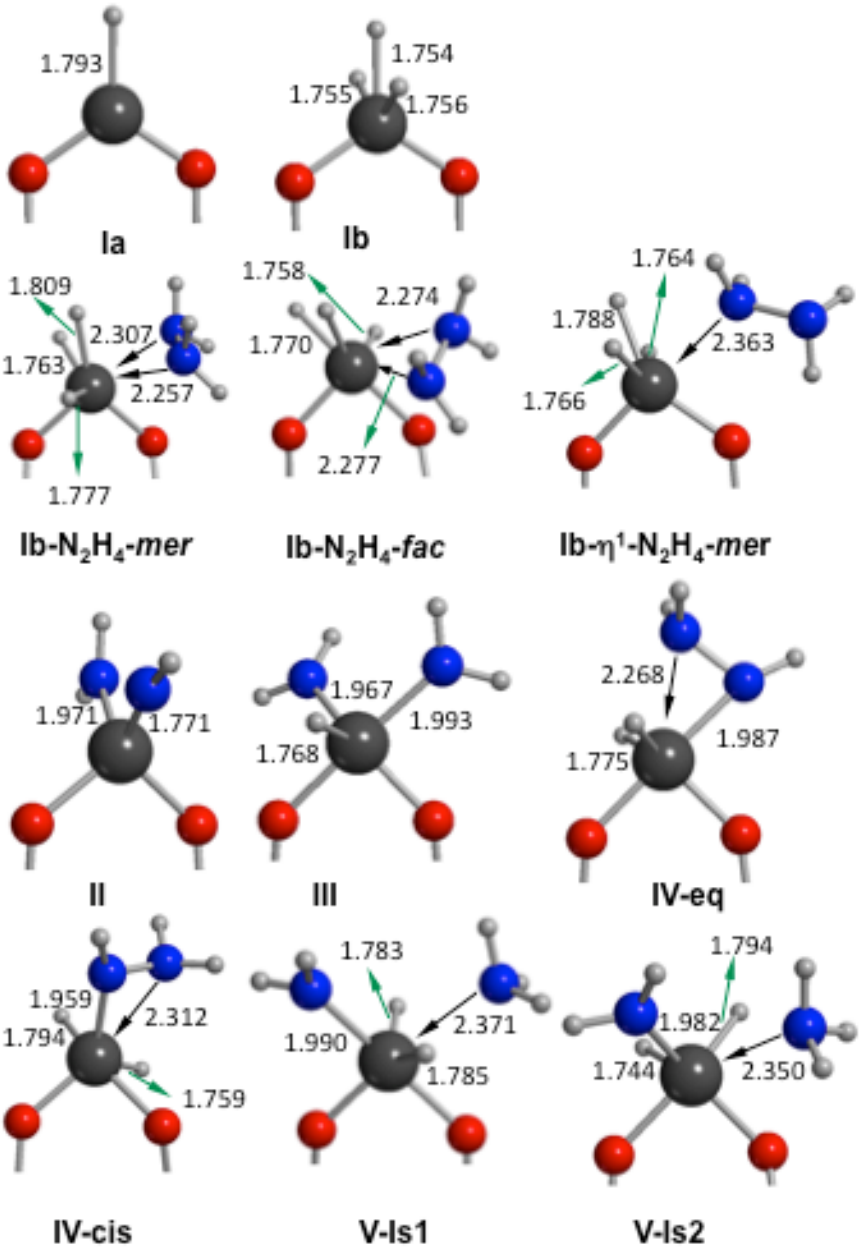


Figure S8. Structures and selected distances in Å for all intermediates involved in the reaction of N_2H_4 with **1b**. Geometries were obtained with a cluster model of the silica surface inside of a 40x40x40Å unit cell, the PBE-D level of theory and the basis sets we used for the CP2K calculations (see computational details section). Black arrows are used for formal donor – acceptor interactions and green arrows for distances.

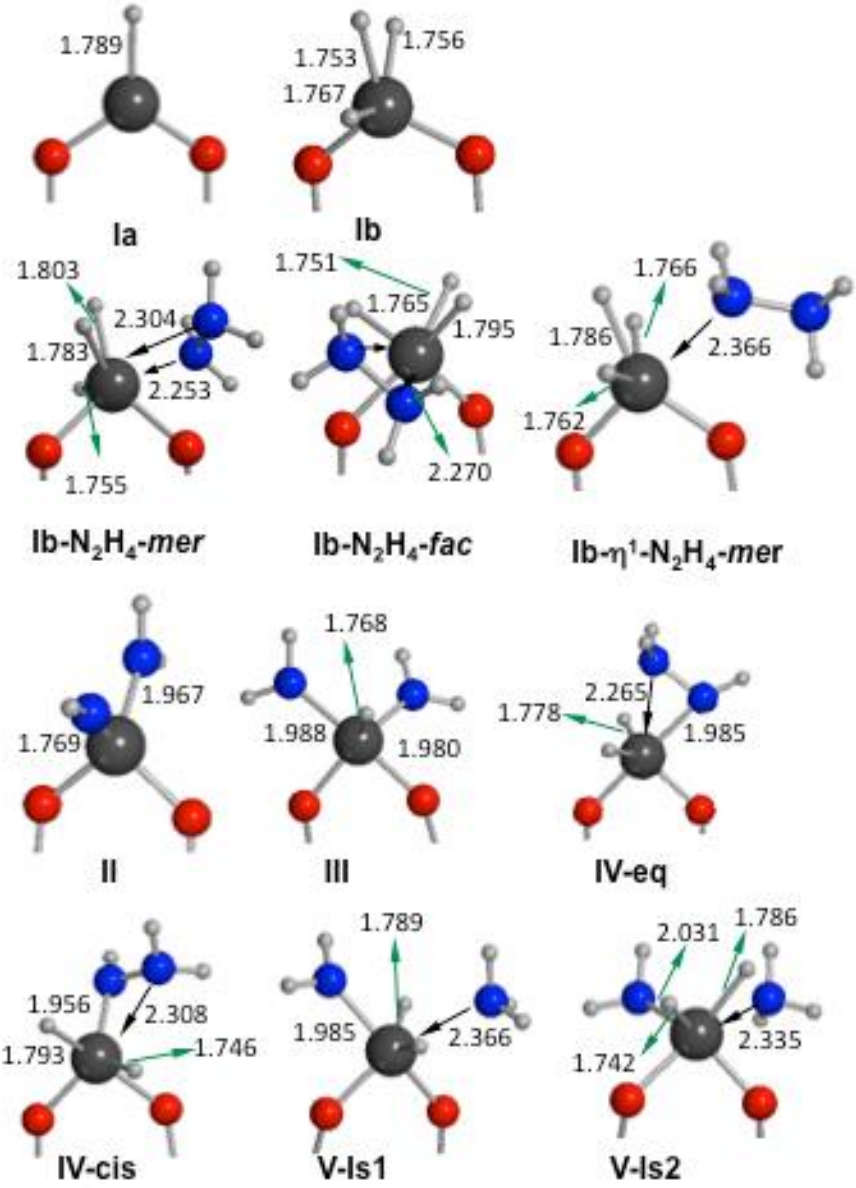


Figure S9. Structures and selected distances in Å for all intermediates involved in the reaction of N_2H_4 with **1b**. Geometries were obtained with the periodic model of the silica surface, the PBE-D level of theory and the basis sets we used for the CP2K calculations (see computational details section). Black arrows are used for formal donor – acceptor interactions and green arrows for distances.

References:

1. Avenier, P.; Taoufik, M.; Lesage, A.; Solans-Monfort, X.; Baudouin, A.; de Mallmann, A.; Veyre, L.; Basset, J.-M.; Eisenstein, O.; Emsley, L.; Quadrelli, E. A. *Science* **2007**, *317*, 1056–1060.
2. Hale, C. F. ; Shetterly, F. F. *J. Amer. Chem. Soc.* **1911**, *33*, 1071-1076.