

## Supporting Information for:

### Enclathration and Confinement of Small Gases by the Intrinsically 0D Porous Molecular Solid, **Me,H,SiMe<sub>2</sub>**

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## 1. General Methods

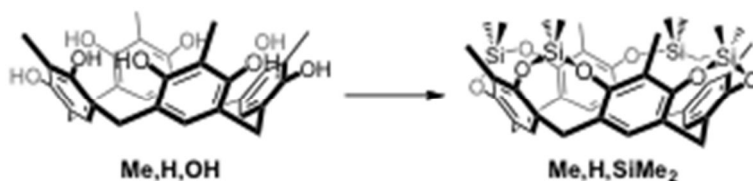
All solvents were used as received from Fisher (Pittsburg, PA). Reagents were obtained from Acros (Pittsburgh, PA) or Aldrich (Milwaukee, WI) and were used without further purification. Chromatography was carried out on silica gel (32-64 $\mu$ m) from Silicycle Chemical Division. For the characterization of the compounds,  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) NMR spectra were carried out on a Varian 400-MR spectrometer at 9.4 T. MestReNova version 5.2.5-4119 software was used for data analysis. Deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. Unless otherwise noted, these spectra were obtained at room temperature and chemical shifts given are based upon on the residual solvent peaks. Splitting patterns are labeled as singlet (s), doublet (d), triplet (t) and broad (br.). Encapsulated species are indicated by preceding an @ symbol.

### Thermogravimetric Analysis (TGA) and TGA tandem mass spectrometry (TGA-MS)

TGA and TGA-MS data were obtained using a TA Instruments Q500 or a TA Instruments Q5000IR TGA coupled to a Pfeiffer Vacuum ThermoStar D-35614 Aslar GSD 300 T3 mass spectrometer for off-gas analysis. Unless otherwise indicated, samples were placed in open platinum pans and heated at a rate of 5°C/min under a constant flow of dry helium (10 mL/min.). Notably, several samples—especially those of guests of relatively large mass or those with mass losses at higher temperatures—consistently appeared to lose more than the expected mass based upon their crystal structures, NMR analyses, or  $x \leq 1$  stoichiometries, yet they are confirmed by PXRD analysis to be pure crystalline phases of  $x(\text{guest})@\text{Me}_2\text{H}_2\text{SiMe}_2$  ( $x \leq 1$ ), isostructural to empty  $\text{Me}_2\text{H}_2\text{SiMe}_2$ . Thus, for some clathrates, reproducibility was an issue due to an apparently violent decomposition of samples occurring upon guest loss, inducing co-sublimation of the host and/or causing particles to be expelled from the TGA pans during analysis. For some samples, better reproducibility could be achieved by grinding the sample to a fine powder prior to analysis. In all cases, reproducible TGAs could be obtained by first sealing the samples in a closed-lid, tared DSC pan and puncturing the DSC pan lid prior to TGA analysis (the “DSC pan technique”, as labeled), though this technique was not applied to all TGA or TGA-MS measurements.

## 2. Synthesis of $\text{Me}_2\text{H}_2\text{SiMe}_2$

Calix[4]resorcinarene  $\text{Me}_2\text{H}_2\text{OH}$  was prepared by a literature method.<sup>S1</sup> Cavitand  $\text{Me}_2\text{H}_2\text{SiMe}_2$  was prepared as follows, analogous to the procedure outlined by Gibb *et al.* for the synthesis of related cavitands,<sup>S2</sup> and was first reported by Lara-Ochoa *et al.*<sup>S3</sup>



$x(\text{H}_2\text{O})@\text{Me}_2\text{H}_2\text{SiMe}_2$  ( $x(\text{H}_2\text{O})@\text{C}_{40}\text{H}_{48}\text{O}_8\text{Si}_4$ )

Under  $\text{N}_2$  atmosphere, calix[4]resorcinarene  $\text{Me}_2\text{H}_2\text{OH}$  (3.0 g, 5.5 mmol) was dissolved in pyridine (180 mL), dichlorodimethylsilane (7.11 g, 6.64 mL, 55.1 mmol) was rapidly added and the mixture was stirred for 48 hours at room temperature. The solvent was then removed *in vacuo* and methanol was added (250 mL) to quench any unreacted  $\text{Cl}_2\text{SiMe}_2$  and the solvent was removed by rotary evaporation. The material was triturated with methanol and the off-white solid was removed by filtration and dried. The crude material was then dissolved in chloroform and passed through a silica gel plug to give, after

evaporation of the solvent, the pure product as a partial hydrate in 68% yield (1.45 g, 1.88 mmol). M.P. = 320-322°C (onset of sublimation). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.16 (s, 4H, ArH<sub>bottom</sub>), 4.26 (d, <sup>2</sup>J<sub>HH</sub> = 13.1 Hz, 4H, CH<sub>2(out)</sub>), 3.35 (d, <sup>2</sup>J<sub>HH</sub> = 13.1 Hz, 4H, CH<sub>2(in)</sub>), 1.93 (s, 12H, ArCH<sub>3</sub>), 0.52 (s, 12H, SiCH<sub>3(out)</sub>), -0.63 (s, 12H, SiCH<sub>3(in)</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.63, 128.09, 127.03, 119.76, 32.25, 10.33, -3.03, -6.23 ppm.

### 3. X-ray Crystallography

CCDC depository numbers 895245-895275, 895459-895460, 943822-943823, 944684, 944828, 948998, 951980, 954924, 956147, 968228, 1415607 contain the single crystal X-ray structure data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

#### Data collection and structure determination

Most single crystal X-ray diffraction data were collected at 100(2) K (or room temperature, as indicated) on a Siemens SMART (or Bruker-AXS) three-circle X-ray diffractometer equipped with a Bruker-AXS APEX II CCD detector and an Oxford Cryosystems 700 Cryostream, using Mo K $\alpha$  radiation (0.71073 Å). Inclusion compounds of CH<sub>3</sub>Br and CH<sub>3</sub>SH were collected at 100(2) K on a Bruker APEX II QUAZAR DUO CCD area-detector diffractometer equipped with an Oxford cryostream and a multilayer monochromator using MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) from an Incoatec I $\mu$ S microsource. The crystal structures were solved by direct methods using SHELXS, and all structural refinements were conducted using SHELXL-97-2.<sup>S4</sup> All non-hydrogen atoms were modeled with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and were refined using a riding model with coordinates and isotropic displacement parameters being dependent upon the atom to which they are attached. The program X-Seed<sup>S6</sup> was used as a graphical interface for the SHELX software suite and for the generation of figures.

#### Guest Occupancy refinement, SQUEEZE refinement, and Occupancy Estimated Standard Deviations (esds)

Guest occupancies were estimated by refinement of the single crystal X-ray diffraction data as follows. Method A. Refined Occupancies (Refined Occ.). Firstly, the atomic positions, occupancy parameters (and anisotropic thermal parameters) of the enclathrated guests were freely refined, with the only constraint being that, for guests with multiple heavy atoms, the occupancies of the enclathrated atoms must all be equal. No geometric constraints were placed on any of the refined guests. The refinements were allowed to converge and the final refined occupancy values are listed in Table S1.

Method B. Individual Occupancies. For clathrates of guests with more than one heavy (non-hydrogen) atom, a separate refinement was performed in which the occupancies of the individual heavy atoms of the guest were refined separately. The refinement was allowed to converge and these values are reported as “Individual Occupancies” in Table S1. Atom 1 is defined as the heavy atom that is deepest in the cavity, followed by atom 2 (next deepest), etc. In this sense, these refinements serve as a validation check for method A and, with the exception of a few structures (e.g., guest = 0.45CO<sub>2</sub>, 0.12EtOH [very low occupancy], 0.75 BrCH<sub>2</sub>Cl [disorder]) generally led to excellent agreement (within 0.04) in the refined occupancy parameters of the individual atoms; the atoms buried more deeply in the cavity generally refined with the smallest thermal parameters and the highest occupancies. No geometric constraints were placed on any of the refined guests. In all cases, the averaged atom occupancies

obtained by this method agreed well with the value obtained from method A. Differences between the individually refined occupancies were generally taken as an estimation of the error in the occupancy estimate (esds).

Method C. SQUEEZE Occupancies (Squeeze Occ.). In order to validate the estimated guest occupancies of the unrestrained, atomistic refinement models, a third refinement was performed, using the SQUEEZE subroutine of PLATON<sup>S5</sup> to estimate the *total* electron density within the cavities of  $x(\text{guest})@ \text{Me,H,SiMe}_2$  clathrates (Table S1). The included guest was deleted from the cavity and fully refined before running SQUEEZE. In all cases, the only solvent accessible voids found by the SQUEEZE routine were located within the **Me,H,SiMe<sub>2</sub>** cavities; the SQUEEZE-estimated electron count within these cavities is given in Tables S1, along with the corresponding calculated occupancies based on the chemical composition of the respective guest. The occupancy values estimated by SQUEEZE were in all cases in excellent agreement with refined values from the methods above.

Further Validation and Reproducibility. Additional steps were taken to validate the clathrate occupancies. For example, for each structure determination, we also adopted a temporary refinement model where the occupancies and thermal parameters of 2-3 arbitrarily chosen heavy atoms of the **Me,H,SiMe<sub>2</sub>** cavitand were freely refined. In all such cases, the occupancies converged to values of  $1.00 \pm 0.03$ . Also, for several samples (e.g.,  $0.79\text{Xe}@ \text{Me,H,SiMe}_2$ ,  $0.58\text{C}_2\text{H}_6@ \text{Me,H,SiMe}_2$ ,  $0.50\text{Kr}@ \text{Me,H,SiMe}_2$ ,  $0.65\text{C}_2\text{H}_4@ \text{Me,H,SiMe}_2$ ,  $\text{CH}_3\text{Cl}@ \text{Me,H,SiMe}_2$ , and  $0.80\text{CH}_3\text{F}@ \text{Me,H,SiMe}_2$ ) occupancies were estimated in the above way for *multiple* SCXRD data collections on *different crystals from the same batch preparation*, or crystals from different batches prepared in the same way. In all cases, single crystal structure determinations on crystals grown by the “defined pressure method” or “atmospheric pressure method” gave guest fractional occupancies, from crystal to crystal, that were statistically identical to the reported structure. Crystals grown by the “General Pressure Method”, gave occupancies that, from crystal to crystal, appeared to be less reproducible. For crystals grown by this method, the occupancy differences from crystal to crystal are suspected to be an indication of inhomogeneity in the sample as the pressure is not constant during crystal growth under these conditions. Some crystals were re-analyzed by SCXRD (same crystal) after a specified period of time of storage under room temperature conditions (stored either in vials at ambient conditions, or in a desiccator), and showed no statistically significant change in their fractional guests occupancies after storage (e.g.,  $0.79(6)\text{CH}_4@ \text{Me,H,SiMe}_2$  and  $0.84(8)\text{CH}_4@ \text{Me,H,SiMe}_2$ , after 5 days;  $0.61(4)\text{CH}_2=\text{CH}_2@ \text{Me,H,SiMe}_2$  and  $0.65(4)\text{C}_2\text{H}_4@ \text{Me,H,SiMe}_2$ , after 11 days;  $0.58(1)\text{C}_2\text{H}_6@ \text{Me,H,SiMe}_2$  and  $0.58(1)\text{C}_2\text{H}_6@ \text{Me,H,SiMe}_2$ , after 11 days), illustrating not only the kinetic stability of these clathrates, but also the reproducibility of the individual SCXRD occupancy measurements.

Estimated Standard Deviations of Occupancy. The guest occupancy values estimated from the refinement methods A and C above were average and the standard deviation determined. Where appropriate, this esd value was compared to the esd obtained from the individual atom occupancies (method B). The larger of the esd values was taken as the reported esd. In some instances, these individual occupancies were also factored into determining the standard deviations of the total guest occupancies. Occupancy values determined to be within 3 esds of 1.0 were considered to be ‘fully occupied’ and the SCXRD structures were refined with 100% occupancy.

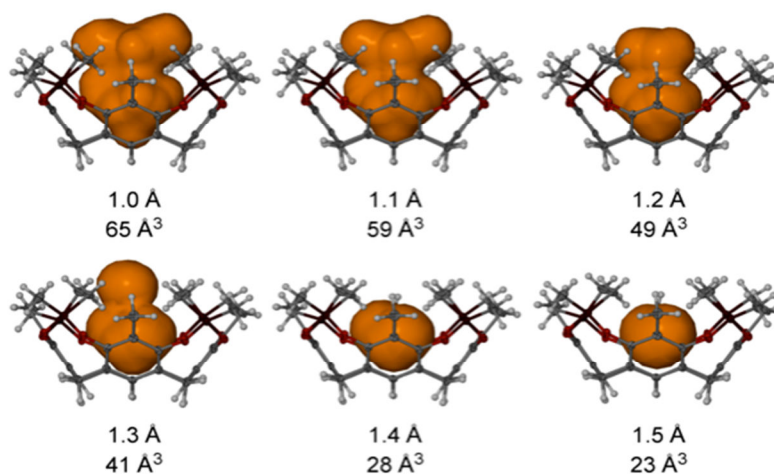
**Supporting Table S1.** Summary of clathrate occupancy determinations by SCXRD.

Guest	Squeeze (e- count)	Squeeze occ.	Refined occ.	Avg occ. (Sq. & Ref.)	esd occ.	Individual Occupancies		
						Atom 1	Atom 2	Atom 3
None <sup>d</sup>	1.63	0.163	0	<b>0.08</b>	<b>0.12</b>			
N <sub>2</sub> (0.34)	4.88	0.35	0.33	<b>0.34</b>	<b>0.02</b>	0.34	0.31	
N <sub>2</sub> (0.23) <sup>a</sup>	3.25	0.23	0.23	<b>0.23</b>	<b>0.02</b>	0.24	0.21	
N <sub>2</sub> (0.14) <sup>a</sup>	2.62	0.19	0.12	<b>0.14</b>	<b>0.05</b>	0.14	0.10	
Ar (0.61)	11.37	0.63	0.58	<b>0.61</b>	<b>0.04</b>			
CH <sub>4</sub> (0.79) <sup>a</sup>	7.38	0.74	0.83	<b>0.79</b>	<b>0.06</b>			
CH <sub>4</sub> (0.84) <sup>a</sup>	7.75	0.78	0.89	<b>0.84</b>				
Kr (0.52)	19.13	0.53	0.51	<b>0.52</b>	<b>0.01</b>			
Kr (0.51) <sup>a</sup>	19.25	0.53	0.49	<b>0.51</b>	<b>0.03</b>			
Kr (0.07) <sup>a</sup>	2.75	0.08	0.07	<b>0.07</b>	<b>0.01</b>			
Xe (0.79)	42	0.78	0.80	<b>0.79</b>				
Xe (0.77)	41	0.75	0.79	<b>0.77</b>				
Xe (0.79)	44	0.81	0.77	<b>0.79</b>				
C <sub>2</sub> H <sub>4</sub> (0.61) <sup>a</sup>	9.375	0.58	0.64	<b>0.61</b>	<b>0.04</b>	0.64	0.65	
C <sub>2</sub> H <sub>4</sub> (0.65) <sup>a</sup>	9.875	0.62	0.68	<b>0.65</b>	<b>0.04</b>	0.68	0.68	
C <sub>2</sub> H <sub>6</sub> (0.58) <sup>a</sup>	10.25	0.57	0.58	<b>0.58</b>	<b>0.01</b>	0.59	0.57	
C <sub>2</sub> H <sub>6</sub> (0.58) <sup>a</sup>	10.5	0.58	0.59	<b>0.58</b>	<b>0.01</b>	0.61	0.57	
C <sub>2</sub> H <sub>6</sub> (0.72)	13	0.72	0.71	<b>0.72</b>	<b>0.02</b>	0.71	0.74	
CH <sub>3</sub> F (0.80)	14	0.83	0.77	<b>0.80</b>	<b>0.04</b>	0.79	0.75	
CH <sub>3</sub> F(0.37),0.14H <sub>2</sub> O <sup>a</sup>	7.75	0.43(nm) <sup>b</sup>	0.37	<b>0.37</b>	<b>nm<sup>b</sup></b>	nm <sup>b</sup>	0.37	
CH <sub>3</sub> F(0.24) <sup>a</sup>	4.5	0.25	0.23	<b>0.24</b>	<b>0.01</b>	0.23	0.23	
CO <sub>2</sub> (0.46) <sup>a</sup>	10	0.45	0.46	<b>0.46</b>	<b>0.06</b>	0.52	0.40	0.45
CO <sub>2</sub> (0.36) <sup>a</sup>	7.5	0.375	0.35	<b>0.36</b>	<b>0.06</b>	0.42	0.32	0.31
CO <sub>2</sub> (0.42)	9.25	0.42	0.42	<b>0.42</b>	<b>0.01</b>	0.43	0.40	0.42
CH <sub>3</sub> Cl	23	0.92	0.87	<b>0.90<sup>b</sup></b>	<b>0.04</b>	0.91	0.86	
CH <sub>3</sub> Cl (fr. EtOAc)	25.25	0.97	0.97	<b>0.98<sup>b</sup></b>	<b>0.01</b>	0.99	0.97	
CH <sub>3</sub> OCH <sub>3</sub> (0.82)	21	0.81	0.82	<b>0.82</b>	<b>0.04</b>	0.88	0.8	0.79
CH <sub>3</sub> CCH (-2CHCl <sub>3</sub> )	23	1.05	1.00	<b>1.02<sup>b</sup></b>	<b>0.02</b>	1.03	1	1.02
CH <sub>3</sub> Br	40	0.93	0.88	<b>0.91<sup>b</sup></b>	<b>0.04</b>	0.95	0.88	
CH <sub>3</sub> SH (0.83)	22	0.85	0.80	<b>0.83</b>	<b>0.04</b>	0.87	0.79	
EtCl	32	0.94	0.95	<b>0.95<sup>b</sup></b>	<b>0.02</b>	0.95	0.96	0.93
CH <sub>2</sub> Cl <sub>2</sub> (0.85) <sup>c</sup>	36	0.86	0.84	<b>0.85</b>	<b>0.01</b>	0.85	0.86	0.84
CH <sub>3</sub> I	61	0.98	0.92	<b>0.95<sup>b</sup></b>	<b>0.03</b>	0.96	0.92	
MeOH	12	0.66	0.68	<b>0.67</b>	<b>0.08</b>	0.76	0.61	
BrCH <sub>2</sub> Cl (0.75) <sup>c</sup>	45	0.75	0.75	<b>0.75</b>	<b>0.00</b>	0.48*	0.67*	1.0*
EtOH (0.13)	3	0.12	0.13	<b>0.13</b>	<b>0.04</b>	0.14	0.2	0.1
MeCN	20	0.95	0.97	<b>0.96<sup>b</sup></b>	<b>0.03</b>	0.98	0.99	1.02
NO <sub>2</sub> CH <sub>3</sub>	30	0.94	0.96	<b>0.95<sup>b</sup></b>	<b>0.05</b>	0.98	0.88	0.95/0.98
H <sub>2</sub> O (0.29) <sup>d</sup>	3	0.3	0.28	<b>0.29</b>	<b>0.01</b>			
H <sub>2</sub> O (0.20) <sup>d</sup>	1.75	0.18	0.21	<b>0.20</b>	<b>0.02</b>			
I <sub>2</sub>	7	0.066	0.06	<b>0.06</b>	<b>0.01</b>	0.07	0.06	
H <sub>2</sub> S (0.85)	15.75	0.875	0.82	<b>0.85</b>	<b>0.04</b>			

<sup>a</sup> These are structure determinations on the same crystal, for the given gas, but after crystal treatment as described in the experimental section. <sup>b</sup> Within 3 esds of 1.0; fixed to be 1.0 for final, reported refinement. <sup>c</sup> disordered guest. <sup>d</sup> Same crystal; partial hydrate single crystal was dehydrated at 150°C and rehydrated in a humidity chamber for ~ two weeks.

### Cavity Volumes, $V_{\text{cav}}$

Cavity volumes are usually extracted from atomic coordinate data by computationally probing the cavity with a sphere of a defined probe radius. The volume of space that can be encompassed by rolling the sphere about the interior of the cavity is summed over all achievable positions of the sphere. The atomic coordinates may be provided by computational or experimental data. For structures of **Me,H,SiMe<sub>2</sub>**, crystal structure data were used with normalized C-H bond lengths of 1.08 Å. Cavity volumes were calculated using the X-seed<sup>S6</sup> interface to MSRoll<sup>S7</sup>, employing the default van der Waals atomic radii and a particular probe radius. The Connolly surfaces are imaged below in orange (Figure S1) and display the void space calculated for a range of probe radii. Notably that there is a significant increase in apparent cavity volume when probed with a 1.3 Å as compared to a 1.4 Å sphere. Thus, it can be understood that a very small change in conformation of the O-Si(Me<sub>2</sub>)-O linkages—inducing a relatively insignificant change to the crystal packing—may drastically affect  $V_{\text{cav}}$ . The probe radius of 1.4 Å (van der Waals radius of a helium atom) was chosen for void space calculations ( $V_{\text{cav}}$ ).



**Supporting Figure S1.** Thermal ellipsoid plots (50%) of **Me,H,SiMe<sub>2</sub>** with Connolly surface diagrams (orange) and various probe radii depicting void space available (C-H bonds normalized to 1.08 Å).

Recognizing that the partial occupancy clathrates are in fact solid solutions of empty and occupied cavitands, and that the cavity volumes estimated by MSRoll ( $V_{\text{MSRoll}}$ ; 1.4 Å probe radius) are therefore a weighted average of the empty **Me,H,SiMe<sub>2</sub>** cavity volume ( $V_{\text{cav}}(\text{empty}) = 28 \text{ \AA}^3$ ) and the volume of the occupied cavities ( $V_{\text{cav}}$ ) in the crystal, the following formula was used to estimate  $V_{\text{cav}}$  from the  $x(\text{guest})@ \text{Me,H,SiMe}_2$  ( $x \leq 1$ ) structures. Where multiple structures of a given gas clathrate were available, the reported  $V_{\text{cav}}$  values represent an average of the values obtained from the different SCXRD data collections.

$$V_{\text{cav}} = [V_{\text{MSRoll}} - (1 - x)V_{\text{cav}}(\text{empty})]/x = [V_{\text{MSRoll}} - 28(1 - x)]/x \text{ \AA}^3$$

### $\text{PF}_{\text{cav}}$

The packing fraction of the guests within the cavitand cavities were calculated using the van der Waals volumes of each guest ( $V_{\text{guest}}$ ) and dividing by their respective  $V_{\text{cav}}$  values.  $\text{PF}_{\text{cav}} = V_{\text{guest}}/V_{\text{cav}}$

## Single Crystal to Single Crystal (SC-SC) H<sub>2</sub>O and CO<sub>2</sub> Sorption Study

### H<sub>2</sub>O

Single crystals of partial cavitand hydrates  $x(\text{H}_2\text{O})@ \text{Me}_2\text{H}_2\text{SiMe}_2$  were obtained by slow evaporation of **Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** from wet chloroform solution. The crystals were completely emptied by placing in an oven at 150°C for several days. Multiple similarly sized crystals were analyzed by single crystal X-ray diffraction at 100(2) K. Data collections ( $t = 0$ ) confirmed the complete absence of electron density within the cavities. For example, for the crystal selected for study of water vapor sorption kinetics, (1.25×1.18×0.66 mm), the largest peak in the difference Fourier map that could be found within the cavity (peak #5, significantly off-center) registered only 0.19 e<sup>-</sup>/Å<sup>3</sup>, establishing that the crystal was in fact empty. This empty crystal was sealed in an evacuated vacuum desiccator containing a pool of liquid water. The crystal was removed periodically from the desiccator for 100(2) K data collections by single crystal X-ray diffraction and was then immediately placed back into the desiccator following data collection. Only after 5 hours in the hydration chamber did the crystal begin to show any sign of water sorption as analyzed by SCXRD at 100 K (peak #13, 0.3 e<sup>-</sup>/Å<sup>3</sup>, centrally located, ascribed to ~0.038 H<sub>2</sub>O). The experiment was repeated at different time intervals and Table S2 below gives the refined oxygen occupancy parameter as a function of time spent by the crystal in the presence of only water vapor ( $P_{\text{H}_2\text{O}}(\text{est.}) = 0.028(3)$  bar, room temperature). Control experiments on a separate empty crystal revealed that simple exposure to atmospheric air (or the low temperature N<sub>2</sub> stream for several hours) over the time scale that the crystal was removed from the desiccator for crystal mounting (less than two hours in total) resulted in no measurable uptake of water or atmospheric gases, as indicated by no measurable electron density within the cavitand cavities of the crystal. With the exception of the water occupancy values, the crystal structures determined in this experiment are redundant with the two other reported partial hydrates and the empty **Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** structure that have been deposited with the CCDC (CCDC depository numbers 895246, 895247, 895248). Thus, they were not deposited in the CCDC; the data is available upon request.

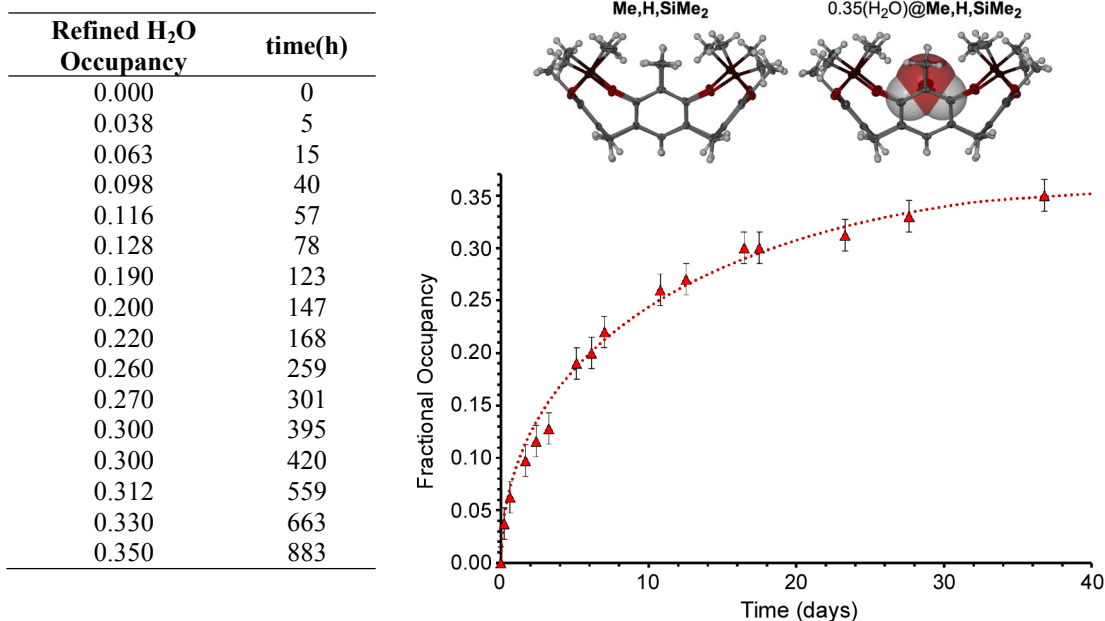
The data were analytically fit to different deceleratory kinetic models (D1, D2, D3, D4, F1, *etc.*), the best fit being obtained for the Ginstling-Brounshtein 3D diffusion model (D4)<sup>S8</sup>:

$$1 - 2\alpha/3 - (1 - \alpha)^{2/3} = kt \quad (\text{D4}),$$

where  $k$ , is the rate constant (hr<sup>-1</sup>),  $t$  is time, and  $\alpha$  is the fraction of conversion to the equilibrium occupancy. The D4 3D diffusion model suggests a mechanism that is consistent with the single-crystal-to-single-crystal hydration process. The fit allowed determination of the rate constant,  $k$ , and the equilibrium occupancy, converging to values of  $k = 3.45(13) \times 10^{-4}$  hr<sup>-1</sup> and an equilibrium occupancy of 0.352(2), corresponding to  $\alpha = 1$ .



**Supporting Table S2 and Figure S2.** Occupancy data for water vapor sorption by a single crystal of **Me,H,SiMe<sub>2</sub>** (1.25×1.18×0.66 mm) at room temperature (est.  $P_{\text{H}_2\text{O}} = 0.028(3)$  bar). The data is plotted as fractional occupancy vs. time (hours) with error bars 1.5% above and below the occupancy determined by SCXRD. Thermal ellipsoid plots (50% probability level) are of the same crystal before exposure to water vapor (left – **Me,H,SiMe<sub>2</sub>**) and at the conclusion of the single crystal sorption experiment (right – **0.35(H<sub>2</sub>O)@Me,H,SiMe<sub>2</sub>**).



## CO<sub>2</sub>

Single crystals of partial cavitand hydrates  $x(\text{H}_2\text{O})@\text{Me,H,SiMe}_2$  were obtained by slow evaporation of **Me,H,SiMe<sub>2</sub>** from wet chloroform solution. The crystals were completely emptied by placing in an oven at 150°C for several days. Multiple similarly sized crystals were analyzed by single crystal X-ray diffraction at 100(2) K. Data collections ( $t = 0$ ) confirmed the complete absence of electron density within the cavities. For example, for the crystal selected for study of water vapor sorption kinetics, (0.57×0.55×0.40 mm), the largest peak in the difference Fourier map that could be found within the cavity (peak #14) registered only  $0.26 \text{ e}^-/\text{\AA}^3$ , establishing that the crystal was in fact empty. This empty crystal was placed in a stainless steel bomb vessel in the presence of 3 Å molecular sieves under 25 bar of carbon dioxide. The crystal was removed periodically from the bomb for 100(2) K data collections by single crystal X-ray diffraction and was then immediately placed back into the bomb following data collection. Within 17 hours in the bomb under pressure did the crystal begin to show any sign of carbon dioxide sorption as analyzed by SCXRD at 100 K (peak #1 ( $0.39 \text{ e}^-/\text{\AA}^3$ ), peak #34 ( $0.24 \text{ e}^-/\text{\AA}^3$ ), and peak #37 ( $0.23 \text{ e}^-/\text{\AA}^3$ ) ascribed to  $\sim 0.030 \text{ CO}_2$ ). The experiment was repeated at different time intervals and Table S3 below gives the refined carbon dioxide occupancy parameter as a function of time spent by the crystal in the presence of only carbon dioxide ( $P_{\text{CO}_2}(\text{est.}) = 25.0(1)$  bar, room temperature). Like above, control experiments on a separate empty crystal revealed that simple exposure to atmospheric air (or the low temperature N<sub>2</sub> stream for several hours) over the time scale that the crystal was removed from the

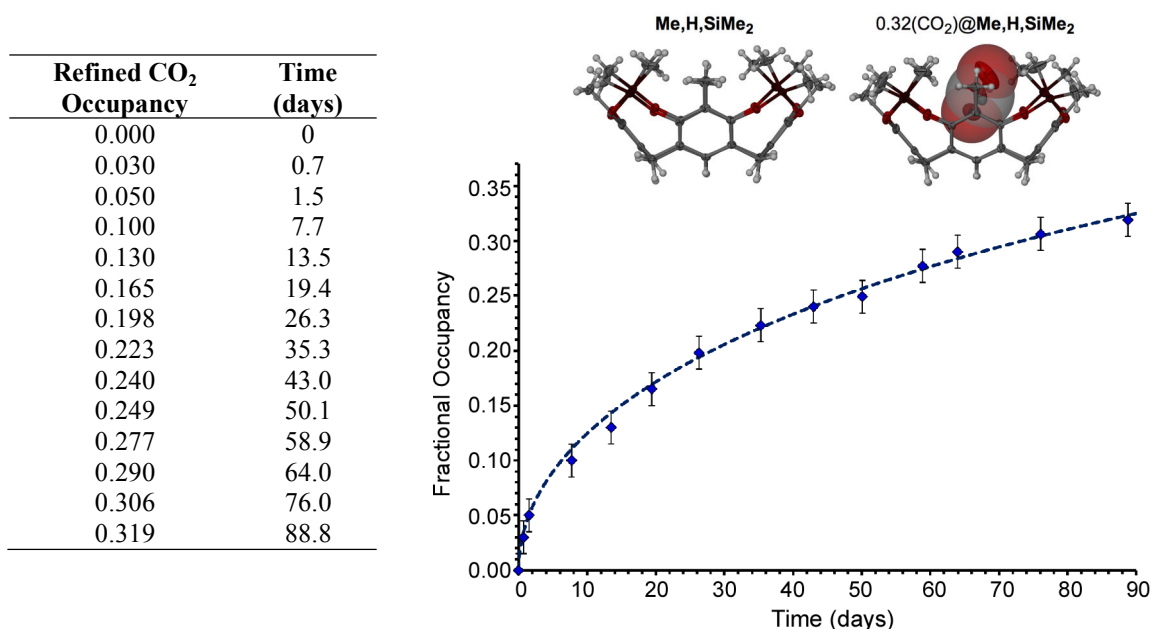
desiccator for crystal mounting (less than two hours in total) resulted in no measurable uptake of water or atmospheric gases, as indicated by no measurable electron density within the cavitand cavities of the crystal. With the exception of the carbon dioxide occupancy values, the crystal structures determined in this experiment are redundant with the two other reported carbon dioxide/cavitand clathrates and the empty **Me,H,SiMe<sub>2</sub>** structure that have been deposited with the CCDC (CCDC depository numbers 895270, 895460, 895245). Thus, they were not deposited in the CCDC; the data is available upon request. Thermal ellipsoid plots (50% probability level) of each CO<sub>2</sub> clathrate of **Me,H,SiMe<sub>2</sub>** during the experiment has instead been presented and are shown in supporting figure SX.

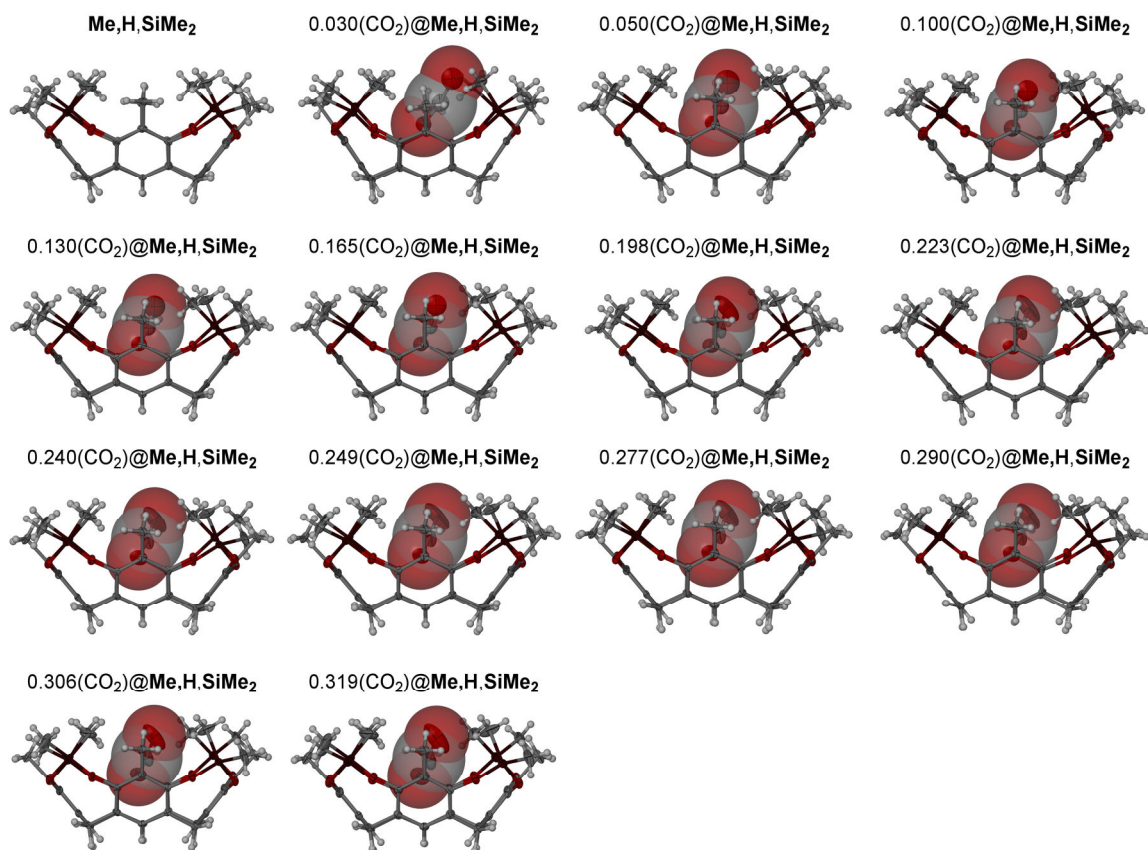
The data were analytically fit to different deceleratory kinetic models (D1, D2, D3, D4, F1, *etc.*), the best fit being obtained for the Ginstling-Brounshtein 3D diffusion model (D4)<sup>S8</sup>:

$$1-2\alpha/3-(1-\alpha)^{2/3} = kt \quad (\text{D4}),$$

where  $k$ , is the rate constant ( $\text{hr}^{-1}$ ),  $t$  is time, and  $\alpha$  is the fraction of conversion to the equilibrium occupancy. The D4 3D diffusion model suggests a mechanism that is consistent with the single-crystal-to-single-crystal hydration process. The fit allowed determination of the rate constant,  $k$ , and the equilibrium occupancy, converging to values of  $k = 3.32(97) \times 10^{-5} \text{ hr}^{-1}$  and an equilibrium occupancy of 0.495(58), corresponding to  $\alpha = 1$ .

**Supporting Table S3 and Figure S3.** Occupancy data for carbon dioxide sorption by a single crystal of **Me,H,SiMe<sub>2</sub>** (0.57×0.55×0.40 mm) at room temperature (est.  $P_{\text{CO}_2} = 25.0(1)$  bar). The data is plotted as fractional occupancy vs. time (days) with error bars 1.5% above and below the occupancy determined by SCXRD. Thermal ellipsoid plots (50% probability level) are of the same crystal before pressurization with CO<sub>2</sub> (left – **Me,H,SiMe<sub>2</sub>**) and at the conclusion of the single crystal sorption experiment (right – 0.32(CO<sub>2</sub>)@**Me,H,SiMe<sub>2</sub>**).





**Supporting Figure S4.** Thermal ellipsoid plots of  $x(\text{CO}_2)@\text{Me,H,SiMe}_2$  clathrates used for the  $\text{CO}_2$  single crystal to single crystal sorption study above, shown at the 50% probability level. (Colors: gray – carbon, red – oxygen, maroon – silicon, white – hydrogen.)

**Supporting Table S4. Crystallographic data for  $x(\text{guest})@ \text{Me}_2\text{H}_2\text{SiMe}_2$ .**

Crystal Parameters	<b>Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub><sup>a</sup></b>	<b>Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub><sup>b</sup></b>	<b>0.21(H<sub>2</sub>O) @Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub><sup>a</sup></b>	<b>0.29(H<sub>2</sub>O) @Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub><sup>a</sup></b>
Chemical formula	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>40</sub> H <sub>48.44</sub> O <sub>8.21</sub> Si <sub>4</sub>	C <sub>40</sub> H <sub>48.58</sub> O <sub>8.29</sub> Si <sub>4</sub>
Formula weight, g/mol	769.14	769.14	772.52	774.36
Growth Solvent	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
Z	8	8	8	8
<i>a</i> , Å	23.8783(24)	23.9089(29)	23.8959(28)	23.8634(18)
<i>b</i> , Å	8.3377(9)	8.4216(10)	8.3362(10)	8.3296(6)
<i>c</i> , Å	42.1053(43)	42.4092(51)	42.0987(49)	42.0507(32)
$\alpha$ , deg	90	90	90	90
$\beta$ , deg	100.631(1)	100.5216(16)	100.506(1)	100.508(1)
$\gamma$ , deg	90	90	90	90
<i>V</i> , Å <sup>3</sup>	8238.9(15)	8395.6(17)	8245.5(17)	8218.3(11)
$\rho_{\text{calc}}$ , g/cm <sup>3</sup>	1.24	1.22	1.24	1.25
crystal dimensions, mm	1.6 x 1.5 x 0.96	0.82 x 0.63 x 0.36	1.6 x 1.5 x 0.96	1.6 x 1.5 x 0.96
<i>T</i> , K	100(2)	298(2)	100(2)	100(2)
2 $\theta$ max for refinement, deg	56.0	56.0	56.0	56.0
total reflections	34790	32862	35218	31061
independent reflections	9663	9999	9652	9631
no. of observed data	7341	6373	6795	7794
no. of parameters	481	481	490	490
<i>R</i> <sub>int</sub>	0.0459	0.0424	0.1154	0.0365
$\mu$ , mm <sup>-1</sup>	0.193	0.190	0.194	0.195
<i>R</i> <sub>1</sub> ( <i>F</i> ), <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ), ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0472, 0.1308	0.0508, 0.1389	0.0474, 0.1145	0.0447, 0.1148
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.065	1.047	0.956	0.854
CCDC Depository Number	895245	895246	895247	895248

<sup>a</sup>Same crystal: 0.21(H<sub>2</sub>O)@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> dehydrated at 150°C to give Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> and then rehydrated to give 0.29(H<sub>2</sub>O)Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> (see text). <sup>b</sup>Note: room temperature data. <sup>c</sup>Note: polymorph.

**Supporting Table S4 (continued). Crystallographic data for  $x(\text{guest})@ \text{Me}_2\text{H}_2\text{SiMe}_2$ .**

Crystal Parameters	<b>CH<sub>3</sub>I@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub></b>	<b>CH<sub>3</sub>Br@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub></b>	<b>CH<sub>3</sub>Cl@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub></b>	<b>CH<sub>3</sub>Cl@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub></b>
Chemical formula	C <sub>41</sub> H <sub>53</sub> O <sub>8</sub> Si <sub>4</sub> I	C <sub>41</sub> H <sub>53</sub> O <sub>8</sub> Si <sub>4</sub> Br	C <sub>41</sub> H <sub>51</sub> O <sub>8</sub> Si <sub>4</sub> Cl	C <sub>41</sub> H <sub>51</sub> O <sub>8</sub> Si <sub>4</sub> Cl
Formula weight, g/mol	911.08	864.09	819.63	819.63
Growth Solvent	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	EtOAc
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
Z	8	8	8	8
<i>a</i> , Å	23.7418(15)	23.7815(29)	23.8190(24)	23.7820(26)
<i>b</i> , Å	8.3761(5)	8.3577(10)	8.3375(9)	8.3354(9)
<i>c</i> , Å	42.6673(28)	42.3173(52)	42.2158(43)	42.2278(46)
$\alpha$ , deg	90	90	90	90
$\beta$ , deg	99.403(1)	98.998(2)	99.032(1)	98.903(1)
$\gamma$ , deg	90	90	90	90
<i>V</i> , Å <sup>3</sup>	8371.0(9)	8307.4(17)	8279.7(15)	8270.1(16)
$\rho_{\text{calc}}$ , g/cm <sup>3</sup>	1.47	1.38	1.32	1.32
crystal dimensions, mm	0.60 x 0.42 x 0.27	0.23 x 0.17 x 0.13	1.0 x 0.70 x 0.70	0.53 x 0.20 x 0.20
<i>T</i> , K	100(2)	100(2)	100(2)	100(2)
2 $\theta$ max for refinement, deg	56.0	56.0	56.0	56.0
total reflections	31937	94190	35918	31511
independent reflections	9883	10023	9807	9757
no. of observed data	7621	8773	7609	6732
no. of parameters	500	500	500	500
<i>R</i> <sub>int</sub>	0.0464	0.0538	0.0517	0.0658
$\mu$ , mm <sup>-1</sup>	0.930	1.156	0.259	0.259
<i>R</i> <sub>1</sub> ( <i>F</i> ), <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ), ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0514, 0.1279	0.0536, 0.1390	0.0521, 0.1356	0.0481, 0.1040
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.059	1.047	1.059	1.058
CCDC Depository Number	895249	895250	895251	895252

**Supporting Table S4 (continued). Crystallographic data for  $x(\text{guest})@ \text{Me}_2\text{H}_2\text{SiMe}_2$ .**

Crystal Parameters	0.80(CH <sub>3</sub> F) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub>	0.37(CH <sub>3</sub> F), 0.14(H <sub>2</sub> O) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>d,e</sup>	0.23(CH <sub>3</sub> F) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>e</sup>	EtCl @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub>
Chemical formula	C <sub>40.8</sub> H <sub>50.4</sub> O <sub>8</sub> Si <sub>4</sub> F <sub>0.80</sub>	C <sub>40.37</sub> H <sub>49.39</sub> O <sub>8.14</sub> Si <sub>4</sub> F <sub>0.37</sub>	C <sub>40.23</sub> H <sub>48.69</sub> O <sub>8</sub> Si <sub>4</sub> F <sub>0.23</sub>	C <sub>42</sub> H <sub>55</sub> O <sub>8</sub> Si <sub>4</sub> Cl
Formula weight, g/mol	796.37	784.27	776.99	829.80
Growth Solvent	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c
Z	8	8	8	8
a, Å	23.8281(25)	23.8507(27)	23.8346(37)	23.5981(20)
b, Å	8.3065(9)	8.3122(9)	8.3212(13)	8.4762(7)
c, Å	42.1464(44)	42.1008(47)	42.0571(64)	42.8436(35)
α, deg	90	90	90	90
β, deg	99.653(1)	100.069(1)	100.274(2)	99.750(1)
γ, deg	90	90	90	90
V, Å <sup>3</sup>	8223.8(15)	8218.0(16)	8211(2)	8445.9(12)
ρ <sub>calc</sub> , g/cm <sup>3</sup>	1.29	1.27	1.26	1.31
crystal dimensions, mm	1.49 x 0.38 x 0.26	0.86 x 0.67 x 0.29	0.86 x 0.67 x 0.29	0.76 x 0.33 x 0.32
T, K	100(2)	100(2)	100(2)	100(2)
2θ max for refinement, deg	56.0	56.0	56.0	56.0
total reflections	31049	31231	35540	36561
independent reflections	9667	9656	9706	10002
no. of observed data	7337	6756	6612	8407
no. of parameters	500	504	500	509
R <sub>int</sub>	0.0506	0.0567	0.06	0.0311
μ, mm <sup>-1</sup>	0.199	0.197	0.195	0.255
R <sub>1</sub> (F), wR <sub>2</sub> (F <sup>2</sup> ), (I > 2σ(I))	0.0543, 0.1114	0.0501, 0.1218	0.0528, 0.1222	0.0421, 0.1062
Goodness-of-fit on F <sup>2</sup>	1.039	1.121	1.125	1.000
CCDC Depository Number	895253	895254	944684	895255

<sup>d</sup>Different crystal from the same batch as 0.80(CH<sub>3</sub>F)@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>, but after 146 days at ambient conditions. <sup>e</sup> Same crystal, but 0.23(CH<sub>3</sub>F)@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> results from heating of 0.37(CH<sub>3</sub>F), 0.14H<sub>2</sub>O@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> crystal for 4 days at 150°C.

**Supporting Table S4 (continued). Crystallographic data for  $x(\text{guest})@ \text{Me}_2\text{H}_2\text{SiMe}_2$ .**

Crystal Parameters	0.74(BrCH <sub>2</sub> Cl) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub>	0.85(CH <sub>2</sub> Cl <sub>2</sub> ) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub>	0.82(CH <sub>3</sub> OCH <sub>3</sub> ) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub>	0.83(CH <sub>3</sub> SH) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub>	0.06(I <sub>2</sub> ) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub>
Chemical formula	C <sub>40.74</sub> H <sub>59.48</sub> O <sub>8</sub> Si <sub>4</sub> Cl <sub>0.74</sub> Br <sub>0.74</sub>	C <sub>40.85</sub> H <sub>49.7</sub> O <sub>8</sub> Si <sub>4</sub> Cl <sub>1.7</sub>	C <sub>41.64</sub> H <sub>52.92</sub> O <sub>8.82</sub> Si <sub>4</sub>	C <sub>40.83</sub> H <sub>51.32</sub> O <sub>8</sub> Si <sub>4</sub> S <sub>0.83</sub>	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> I <sub>0.12</sub>
Formula weight, g/mol	864.90	841.35	806.94	809.09	784.37
Growth Solvent	BrCH <sub>2</sub> Cl	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c
Z	8	8	8	8	8
a, Å	23.7650(20)	23.8439(22)	23.8115(22)	23.8489(14)	23.8600(12)
b, Å	8.4219(7)	8.3749(8)	8.3707(8)	8.3186(5)	8.3389(4)
c, Å	42.7905(36)	42.7877(39)	42.6458(40)	42.2892(26)	42.1352(22)
α, deg	90	90	90	90	90
β, deg	101.108(1)	101.337(1)	100.829(1)	99.377(1)	100.525(1)
γ, deg	90	90	90	90	90
V, Å <sup>3</sup>	8403.9(12)	8377.6(13)	8348.7(14)	8277.6(9)	8242.4(7)
ρ <sub>calc</sub> , g/cm <sup>3</sup>	1.37	1.33	1.28	1.30	1.26
crystal dimensions, mm	0.82 x 0.43 x 0.21	0.36 x 0.26 x 0.26	0.87 x 0.72 x 0.11	0.47 x 0.15 x 0.11	0.47 x 0.38 x 0.07
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
2θ max for refinement, deg	56.0	56.0	56.0	56.0	56.0
total reflections	35425	36480	31519	109616	35677
independent reflections	9891	9939	9787	9981	9737
no. of observed data	7435	7379	7631	9164	7450
no. of parameters	538	535	510	501	508
R <sub>int</sub>	0.0427	0.0467	0.0459	0.0411	0.042
μ, mm <sup>-1</sup>	0.943	0.301	0.195	0.236	0.283
R <sub>1</sub> (F), wR <sub>2</sub> (F <sup>2</sup> ), (I > 2σ(I))	0.0555, 0.1207	0.0461, 0.1056	0.0522, 0.1197	0.0503, 0.1207	0.0556, 0.1257
Goodness-of-fit on F <sup>2</sup>	1.043	1.052	1.030	1.127	1.057
CCDC Depository Number	895256	895257	895258	895259	951980

**Supporting Table S4 (continued). Crystallographic data for  $x(\text{guest})@ \text{Me}_2\text{H}_2\text{SiMe}_2$ .**

Crystal Parameters	0.72(C <sub>2</sub> H <sub>6</sub> ) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub>	0.58(C <sub>2</sub> H <sub>6</sub> ) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>f,g</sup>	0.58(C <sub>2</sub> H <sub>6</sub> ) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>f,g</sup>	0.77(Xe) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>h</sup>	0.79(Xe) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>h</sup>
Chemical formula	C <sub>41.44</sub> H <sub>52.32</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>41.16</sub> H <sub>51.48</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>41.16</sub> H <sub>51.48</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> Xe <sub>0.77</sub>	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> Xe <sub>0.79</sub>
Formula weight, g/mol	790.79	786.60	786.60	870.24	872.88
Growth Solvent	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c
Z	8	8	8	8	8
a, Å	23.7918(15)	23.8264(18)	23.8337(17)	23.7847(20)	23.7967(66)
b, Å	8.3456(5)	8.3413(6)	8.3490(6)	8.3252(7)	8.3333(23)
c, Å	42.2677(26)	42.2478(32)	42.2611(30)	42.2368(35)	42.2748(117)
α, deg	90	90	90	90	90
β, deg	99.785(1)	99.931(1)	99.898(1)	99.359(1)	99.380(4)
γ, deg	90	90	90	90	90
V, Å <sup>3</sup>	8270.5(10)	8270.7(11)	8284.3(10)	8252.1(12)	8271(4)
ρ <sub>calc</sub> , g/cm <sup>3</sup>	1.27	1.26	1.26	1.40	1.40
crystal dimensions, mm	0.60 x 0.36 x 0.35	0.97 x 0.56 x 0.47	0.97 x 0.56 x 0.47	0.40 x 0.20 x 0.12	0.45 x 0.11 x 0.10
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
2θ max for refinement, deg	56.0	56.0	56.0	56.0	56.0
total reflections	31373	30916	30915	30957	34740
independent reflections	9719	9625	9666	9679	9736
no. of observed data	7880	8089	8501	7851	6908
no. of parameters	501	501	501	490	490
R <sub>int</sub>	0.0383	0.0329	0.031	0.0458	0.0690
μ, mm <sup>-1</sup>	0.194	0.194	0.194	0.815	0.830
R <sub>1</sub> (F), wR <sub>2</sub> (F <sup>2</sup> ), (I > 2σ(I))	0.0500, 0.1104	0.0526, 0.1128	0.0543, 0.1173	0.0559, 0.1061	0.0564, 0.1184
Goodness-of-fit on F <sup>2</sup>	1.062	1.090	1.155	1.160	1.085
CCDC Depository Number	895260	895261	943822	895262	895263

<sup>f</sup>Same crystal, the 2<sup>nd</sup> data collection occurring after 11 days at room temperature in a desiccator. <sup>g</sup>Crystal obtained under 9.8 bar of ethane. <sup>h</sup>Different crystals from the same batch preparation; the latter analyzed after 112 days storage under ambient conditions.

**Supporting Table S4 (continued). Crystallographic data for  $x(\text{guest})@ \text{Me}_2\text{H}_2\text{SiMe}_2$ .**

Crystal Parameters	0.79(Xe)@ Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>i</sup>	0.52(Kr) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>j</sup>	0.51(Kr) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>k</sup>	0.07(Kr) @Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>k</sup>	0.61(Ar)@ Me <sub>2</sub> H <sub>2</sub> SiMe <sub>2</sub> <sup>l</sup>
Chemical formula	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> Xe <sub>0.79</sub>	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> Kr <sub>0.52</sub>	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> Kr <sub>0.51</sub>	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> Kr <sub>0.07</sub>	C <sub>40</sub> H <sub>48</sub> O <sub>8</sub> Si <sub>4</sub> Ar <sub>0.61</sub>
Formula weight, g/mol	872.88	812.74	811.9	775.03	793.53
Growth Solvent	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c
Z	8	8	8	8	8
a, Å	23.8039(31)	23.8065(23)	23.8233(20)	23.8513(17)	23.8044(54)
b, Å	8.3344(11)	8.3338(8)	8.3369(7)	8.3338(6)	8.3353(19)
c, Å	42.2656(54)	42.0866(41)	42.0867(35)	42.0596(30)	42.0675(95)
α, deg	90	90	90	90	90
β, deg	99.346(2)	99.934(2)	99.935(1)	100.528(1)	100.038(4)
γ, deg	90	90	90	90	90
V, Å <sup>3</sup>	8274(2)	8224.7	8233.6(12)	8219.5(10)	8219(3)
ρ <sub>calc</sub> , g/cm <sup>3</sup>	1.40	1.31	1.31	1.25	1.28
crystal dimensions, mm	0.42 x 0.21 x 0.21	0.52 x 0.20 x 0.19	0.49 x 0.14 x 0.11	0.49 x 0.14 x 0.11	0.44 x 0.24 x 0.20
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
2θ max for refinement, deg	56.0	56.0	56.0	56.0	56.0
total reflections	35031	38045	31294	34617	34650
independent reflections	9973	9926	9697	9686	9907
no. of observed data	8883	8418	6728	6517	8038
no. of parameters	490	490	490	490	490
R <sub>int</sub>	0.0516	0.0375	0.0620	0.0691	0.0744
μ, mm <sup>-1</sup>	0.829	0.750	0.738	0.269	0.244
R <sub>1</sub> (F), wR <sub>2</sub> (F <sup>2</sup> ), (I > 2σ(I))	0.0367, 0.0835	0.0377, 0.0838	0.0489, 0.1069	0.0540, 0.1126	0.0479, 0.1176
Goodness-of-fit on F <sup>2</sup>	1.024	1.051	1.040	1.025	1.020
CCDC Depository Number	895269	895266	943823	895267	895268

<sup>i</sup> Crystal obtained under 9.8 bar of xenon. <sup>j</sup> Crystal obtained under 9.8 bar of krypton. <sup>k</sup> Same crystal, but the latter data set being obtained after heating at 100 °C for two weeks. <sup>l</sup> Crystal obtained under 80 bar of argon.

**Supporting Table S4 (continued). Crystallographic data for  $x(\text{guest})@ \text{Me,H,SiMe}_2$ .**

Crystal Parameters	0.61(C <sub>2</sub> H <sub>4</sub> ) @Me,H,SiMe <sub>2</sub> <sup>m,n</sup>	0.65(C <sub>2</sub> H <sub>4</sub> ) @Me,H,SiMe <sub>2</sub> <sup>m,n</sup>	0.46(CO <sub>2</sub> )@ Me,H,SiMe <sub>2</sub> <sup>o</sup>	0.36(CO <sub>2</sub> )@ Me,H,SiMe <sub>2</sub> <sup>o</sup>
Chemical formula	C <sub>41.22</sub> H <sub>50.44</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>41.30</sub> H <sub>50.6</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>40.46</sub> H <sub>48</sub> O <sub>8.92</sub> Si <sub>4</sub>	C <sub>40.36</sub> H <sub>48</sub> O <sub>8.72</sub> Si <sub>4</sub>
Formula weight, g/mol	786.27	787.39	789.4	785.0
Growth Solvent	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c
Z	8	8	8	8
a, Å	23.8542(15)	23.8418(20)	23.9014(24)	23.8910(19)
b, Å	8.3297(5)	8.3261(7)	8.3164(8)	8.3191(7)
c, Å	42.0737(27)	42.0686(35)	41.9864(43)	41.9940(34)
α, deg	90	90	90	90
β, deg	99.530(1)	99.529(1)	100.205(1)	100.294(1)
γ, deg	90	90	90	90
V, Å <sup>3</sup>	8244.6(9)	8235.8(12)	8213.8(14)	8212.03
ρ <sub>calc</sub> , g/cm <sup>3</sup>	1.26	1.27	1.28	1.27
crystal dimensions, mm	0.66 x 0.45 x 0.38	0.66 x 0.45 x 0.38	0.64 x 0.51 x 0.20	0.64 x 0.51 x 0.20
T, K	100(2)	100(2)	100(2)	100(2)
2θ max for refinement, deg	56.0	56.0	56.0	56.0
total reflections	30998	31054	34737	34657
independent reflections	9643	9648	9667	9618
no. of observed data	7747	8333	6967	6696
no. of parameters	511	511	508	508
R <sub>int</sub>	0.0379	0.0291	0.0519	0.0578
μ, mm <sup>-1</sup>	0.195	0.195	0.197	0.197
R <sub>1</sub> (F), wR <sub>2</sub> (F <sup>2</sup> ), (I > 2σ(I))	0.0447, 0.1062	0.0429, 0.1022	0.0475, 0.1130	0.0511, 0.1135
Goodness-of-fit on F <sup>2</sup>	1.018	1.029	1.103	1.098
CCDC Depository Number	895264	895265	895270	895460

<sup>m</sup>Same crystal, the second collection occurring after 11 days at room temperature in a desiccator. <sup>n</sup>Crystal obtained under 9.8 bar of ethylene.<sup>o</sup>Same crystal, the second collection occurring after 10 days under ambient conditions.**Supporting Table S4 (continued). Crystallographic data for  $x(\text{guest})@ \text{Me,H,SiMe}_2$ .**

Crystal Parameters	0.34(N <sub>2</sub> )@ Me,H,SiMe <sub>2</sub>	0.23(N <sub>2</sub> )@ Me,H,SiMe <sub>2</sub> <sup>p,q</sup>	0.14(N <sub>2</sub> )@ Me,H,SiMe <sub>2</sub> <sup>p,q</sup>	0.85(H <sub>2</sub> S)@ Me,H,SiMe <sub>2</sub>	0.13(EtOH)@ Me,H,SiMe <sub>2</sub>
Chemical formula	C <sub>40</sub> H <sub>48</sub> N <sub>0.68</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>40</sub> H <sub>48</sub> N <sub>0.46</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>40</sub> H <sub>48</sub> N <sub>0.28</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>40</sub> H <sub>49.7</sub> O <sub>8</sub> Si <sub>4</sub> S <sub>0.85</sub>	C <sub>40.26</sub> H <sub>48.78</sub> O <sub>8.13</sub> Si <sub>4</sub>
Formula weight, g/mol	778.68	775.6	773.08	798.13	775.15
Growth Solvent	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CHCl <sub>3</sub> /EtOH
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c
Z	8	8	8	8	8
a, Å	23.8734(51)	23.9252(99)	23.8696(29)	23.8283(49)	23.8670(26)
b, Å	8.3386(18)	8.3510(35)	8.3289(10)	8.3023(17)	8.3297(9)
c, Å	42.0966(90)	42.1598(174)	42.0909(51)	42.0931(88)	42.1428(46)
α, deg	90	90	90	90	90
β, deg	100.330(3)	100.429(5)	100.485(2)	99.374(3)	100.399(2)
γ, deg	90	90	90	90	90
V, Å <sup>3</sup>	8244(3)	8284(6)	8228	8216(3)	8240.6(16)
ρ <sub>calc</sub> , g/cm <sup>3</sup>	1.25	1.24	1.25	1.29	1.25
crystal dimensions, mm	0.37 x 0.21 x 0.13	0.90 x 0.26 x 0.08	0.90 x 0.26 x 0.08	0.40 x 0.21 x 0.10	1.11 x 0.61 x 0.27
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
2θ max for refinement, deg	56.0	56.0	56.0	56.0	56.0
total reflections	30323	30833	30843	23652	34883
independent reflections	9540	9649	9620	9360	9766
no. of observed data	7087	7515	7458	6981	6672
no. of parameters	489	489	489	498	495
R <sub>int</sub>	0.0614	0.0378	0.0396	0.0487	0.0605
μ, mm <sup>-1</sup>	0.194	0.193	0.194	0.238	0.194
R <sub>1</sub> (F), wR <sub>2</sub> (F <sup>2</sup> ), (I > 2σ(I))	0.0536, 0.1271	0.0438, 0.1054	0.0451, 0.1042	0.0509, 0.1088	0.0519, 0.1178
Goodness-of-fit on F <sup>2</sup>	1.036	1.040	1.042	1.058	1.068
CCDC Depository Number	895271	954924	956147	944828	895275

<sup>p</sup> A second crystal from the same batch preparation as 0.34(N<sub>2</sub>)@Me,H,SiMe<sub>2</sub>, but after the crystal had been in a desiccator, at room temperature, for 54 hrs and 233 hrs (7days, 17 hrs), respectively. <sup>q</sup> Same crystal.

**Supporting Table S4 (continued). Crystallographic data for  $x(\text{guest})@ \text{Me}_x\text{H}_y\text{SiMe}_2$ .**

Crystal Parameters	0.79(CH <sub>4</sub> ) @Me <sub>0.79</sub> H <sub>49.64</sub> Si <sub>4</sub> <sup>r,s</sup>	0.84(CH <sub>4</sub> ) @Me <sub>0.84</sub> H <sub>49.64</sub> Si <sub>4</sub> <sup>r,s</sup>	CH <sub>3</sub> CN @Me <sub>1</sub> H <sub>51</sub> Si <sub>4</sub> N	NO <sub>2</sub> CH <sub>3</sub> @Me <sub>1</sub> H <sub>51</sub> O <sub>10</sub> Si <sub>4</sub> N	0.67(CH <sub>3</sub> OH) @Me <sub>0.67</sub> H <sub>50.68</sub> O <sub>8.67</sub> Si <sub>4</sub>
Chemical formula	C <sub>40.79</sub> H <sub>49.64</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>40.84</sub> H <sub>49.64</sub> O <sub>8</sub> Si <sub>4</sub>	C <sub>42</sub> H <sub>51</sub> O <sub>8</sub> Si <sub>4</sub> N	C <sub>41</sub> H <sub>51</sub> O <sub>10</sub> Si <sub>4</sub> N	C <sub>40.67</sub> H <sub>50.68</sub> O <sub>8.67</sub> Si <sub>4</sub>
Formula weight, g/mol	781.83	782.64	810.2	830.19	790.61
Growth Solvent	CHCl <sub>3</sub>	CHCl <sub>3</sub>	CH <sub>3</sub> CN	NO <sub>2</sub> CH <sub>3</sub>	CHCl <sub>3</sub> /MeOH
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>Z</i>	8	8	8	8	8
<i>a</i> , Å	23.8394(23)	23.8344(33)	23.8211(29)	23.9220(31)	23.9064(22)
<i>b</i> , Å	8.3267(8)	8.3285(12)	8.3280(12)	8.2830(11)	8.3015(8)
<i>c</i> , Å	42.1921(40)	42.1886(59)	42.0611(62)	42.4669(54)	42.1497(39)
$\alpha$ , deg	90	90	90	90	90
$\beta$ , deg	99.767(1)	99.798(2)	98.894(2)	100.387(1)	100.301(1)
$\gamma$ , deg	90	90	90	90	90
<i>V</i> , Å <sup>3</sup>	8253.9(14)	8252(2)	8244(2)	8276.7(19)	8230.2(13)
$\rho_{\text{calc}}$ , g/cm <sup>3</sup>	1.26	1.26	1.31	1.33	1.28
crystal dimensions, mm	1.77 x 0.64 x 0.50	1.77 x 0.64 x 0.50	0.41 x 0.13 x 0.13	0.45 x 0.42 x 0.41	0.45 x 0.42 x 0.41
<i>T</i> , K	100(2)	100(2)	100(2)	100(2)	100(2)
2 $\theta$ max for refinement, deg	56.0	56.0	56.0	56.0	56.0
total reflections	30957	30782	35116	35023	34888
independent reflections	9621	9601	9620	9736	9732
no. of observed data	7757	7858	6335	8235	6601
no. of parameters	490	490	509	518	501
<i>R</i> <sub>int</sub>	0.0384	0.0357	0.0728	0.0298	0.0636
$\mu$ , mm <sup>-1</sup>	0.194	0.194	0.197	0.202	0.196
<i>R</i> <sub>1</sub> ( <i>F</i> ), w <i>R</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ), ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0442, 0.1112	0.0441, 0.1096	0.0554, 0.1222	0.0411, 0.1038	0.0522, 0.1153
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.048	1.030	1.047	1.040	1.078
CCDC Depository Number	895459	968228	895272	895273	895274

<sup>r</sup>Same crystal, the 2<sup>nd</sup> data collection occurring after 5 days at room temperature in a desiccator. <sup>s</sup>Crystal obtained under 36 bar of methane.

**Supporting Table S4 (continued). Crystallographic data for CH<sub>3</sub>CCH@Me<sub>1</sub>H<sub>51</sub>SiMe<sub>2</sub>·2CHCl<sub>3</sub>**

Crystal Parameters	CH <sub>3</sub> CCH@ Me <sub>1</sub> H <sub>51</sub> SiMe <sub>2</sub> ·2CHCl <sub>3</sub>
Chemical formula	C <sub>45</sub> H <sub>54</sub> O <sub>8</sub> Si <sub>4</sub> Cl <sub>6</sub>
Formula weight, g/mol	1047.98
Growth Solvent	CHCl <sub>3</sub>
Crystal system	Monoclinic
Space group	<i>P2<sub>1</sub>/n</i>
<i>Z</i>	4
<i>a</i> , Å	11.6044(23)
<i>b</i> , Å	18.0529(35)
<i>c</i> , Å	24.1294(47)
$\alpha$ , deg	90
$\beta$ , deg	98.247(2)
$\gamma$ , deg	90
<i>V</i> , Å <sup>3</sup>	5002.67
$\rho_{\text{calc}}$ , g/cm <sup>3</sup>	1.39
crystal dimensions, mm	1.1 x 0.56 x 0.35
<i>T</i> , K	100(2)
2 $\theta$ max for refinement, deg	50.0
total reflections	43388
independent reflections	11920
no. of observed data	8650
no. of parameters	581
<i>R</i> <sub>int</sub>	0.0510
$\mu$ , mm <sup>-1</sup>	0.489
<i>R</i> <sub>1</sub> ( <i>F</i> ), w <i>R</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ), ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0698, 0.1935
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.114
CCDC Depository Number	948998



## Cavitand Conformations

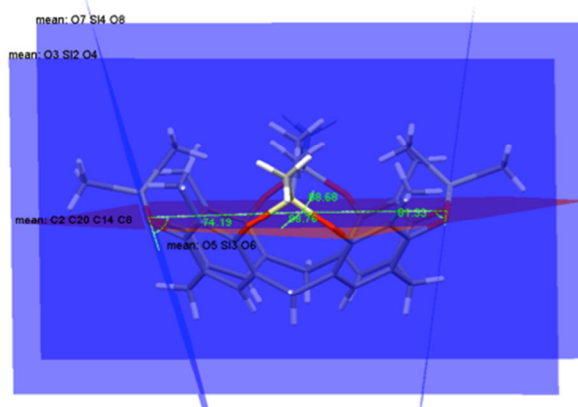
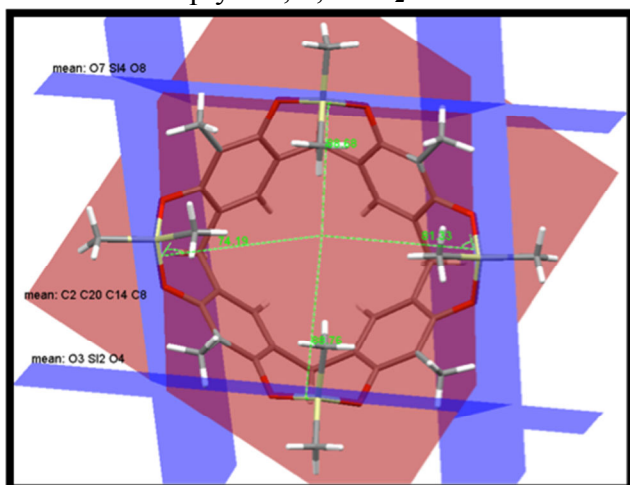
To accommodate larger guests, the cavitand flexes slightly so as to increasing the cavity volume. Swelling of the cavity largely entails a conformational adjustment of the O-Si(Me<sub>2</sub>)-O linkages such that the angles between planes defined by the O-Si-O linkers and the plane defined by the upper rim ( $\tau$ ) carbon atoms becomes more acute. Table S5 gives the four symmetry-unique  $\tau$  angles, their averages, and their difference relative to the empty **Me<sub>3</sub>H<sub>3</sub>SiMe<sub>2</sub>** ( $\Delta\tau$ ) for  $x(\text{guest})@ \text{Me}_3\text{H}_3\text{SiMe}_2$  clathrates. The general trend in the table shows that there is a correlation between increasing  $V_{\text{cell}}$  and  $V_g$  and increasing  $\Delta\tau$ . Figure S2 below shows the defined planes (red/blue) and the angles between said planes (green) for empty **Me<sub>3</sub>H<sub>3</sub>SiMe<sub>2</sub>** and EtCl@**Me<sub>3</sub>H<sub>3</sub>SiMe<sub>2</sub>**.

**Supporting Table S5.** Angles,  $\tau$ , between planes of all O-Si-O functionalities and the plane defined by the upper rim carbon atoms of the arene rings of **Me<sub>3</sub>H<sub>3</sub>SiMe<sub>2</sub>** (see figures for definition of  $\tau$ ).

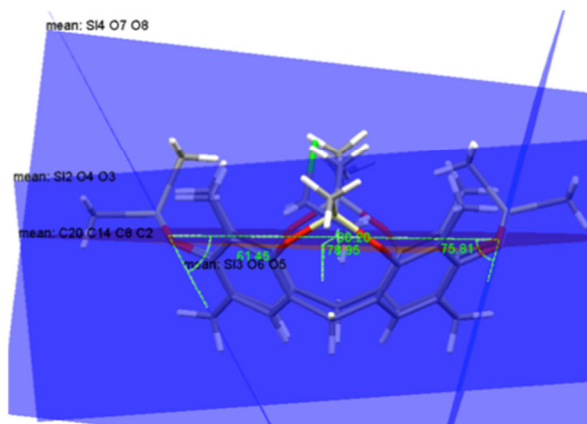
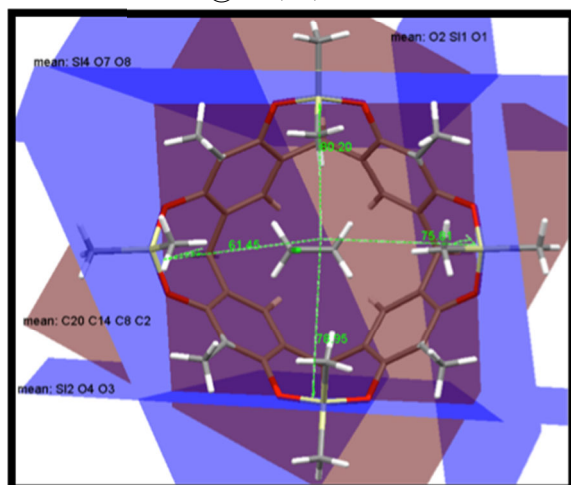
Guest	Angle, $\tau$ (small to large)				Avg. ( $\tau$ )	St. Dev.	$\Delta\tau$ ( $^\circ$ )	$V_g$	$V_{\text{cell}}$
	1	2	3	4					
None	74.16	81.33	88.69	88.77	85.01	5.20	0		8230
0.34N <sub>2</sub>	72.58	80.97	87.27	89.53	82.59	7.59	2.4	22	8244
0.61Ar	72.23	80.86	86.42	88.40	81.98	7.24	3.0	28	8219
0.79CH <sub>4</sub>	71.11	80.10	84.89	86.48	80.65	6.91	4.4	28	8254
0.52Kr	72.51	80.55	85.68	87.73	81.62	6.78	3.4	35	8225
0.77Xe	69.53	78.61	81.37	83.26	78.19	6.08	6.8	42	8252
0.65C <sub>2</sub> H <sub>4</sub>	69.64	80.07	82.98	86.40	79.77	7.23	5.2	40	8236
0.72C <sub>2</sub> H <sub>6</sub>	65.65	79.24	81.42	85.11	77.86	8.49	7.2	45	8275
0.80CH <sub>3</sub> F	71.37	79.70	84.23	86.06	80.34	6.55	4.7	32	8224
0.46CO <sub>2</sub>	68.79	81.25	86.00	89.51	81.39	9.05	3.6	32	8214
1.0CH <sub>3</sub> Cl	66.45	78.72	78.89	83.04	76.78	7.17	8.2	44	8280
0.82CH <sub>3</sub> OCH <sub>3</sub>	58.1	76.9	82.08	83.70	75.20	11.76	9.8	53	8349
1.0CH <sub>3</sub> CCH <sup>a</sup>	74.25	74.31	77.16	80.79	76.63	3.09	8.4	51	5003
1.0CH <sub>3</sub> Br	63.36	77.04	78.17	81.71	75.07	8.06	9.9	49	8307
0.83CH <sub>3</sub> SH	63.63	77.9	78.43	84.05	76.00	8.71	9.0	46	8278
1.0EtCl	61.46	75.8	78.93	80.20	74.10	8.63	10.9	61	8446
0.85CH <sub>2</sub> Cl <sub>2</sub>	56.64	73.6	81.73	82.92	73.72	12.12	11.3	59	8378
1.0CH <sub>3</sub> I	55.88	75.96	77.21	78.76	71.95	10.78	13.1	53	8371
0.67MeOH	69.91	78.37	85.30	87.76	80.34	8.01	4.7	37	8230
0.75ClCH <sub>2</sub> Br	57.27	73.81	82.01	83.29	74.10	11.98	10.9	64	8404
0.13EtOH	72.32	80.86	87.50	89.94	82.66	7.89	2.4	54	8241
1.0MeCN	64.54	78.94	79.01	83.94	76.61	8.38	8.4	44	8244
1.0NO <sub>2</sub> Me	60.62	72.08	81.19	82.52	74.10	10.12	10.9	51	8277
0.29H <sub>2</sub> O	74.43	81.42	88.60	89.22	83.42	6.96	1.6	18	8218
0.06I <sub>2</sub>	72.91	80.7	88.18	89.68	82.87	7.71	2.1	60	8242
0.85H <sub>2</sub> S	71.12	79.8	83.37	84.75	79.76	6.13	5.2	28	8216

<sup>a</sup> From the crystal structure of CH<sub>3</sub>CCH@**Me<sub>3</sub>H<sub>3</sub>SiMe<sub>2</sub>**·2CHCl<sub>3</sub>.

Empty  $\text{Me}_3\text{H}_2\text{SiMe}_2$



$\text{EtCl}@\text{Me}_3\text{H}_2\text{SiMe}_2$



**Supporting Figure S5.** Top and side views of a) empty  $\text{Me}_3\text{H}_2\text{SiMe}_2$  and b)  $\text{EtCl}@\text{Me}_3\text{H}_2\text{SiMe}_2$  showing planes defined by O-Si-O bonds (blue) and by the upper rim carbon atoms of the cavitand arene rings (red) and the corresponding  $\tau$  angles between them, listed in Supporting Table S5.

## 4. Synthesis and Characterization

### Gas Clathrate Preparation Methods

- 1) **Bubbling to Dryness Method.** Preliminary screening of gas capture (at ambient pressure) by **Me,H,SiMe<sub>2</sub>** was performed as follows. Saturated solutions of empty **Me,H,SiMe<sub>2</sub>** in chloroform (solubility ~80 mg/mL) were prepared and selected protic gases were continuously passed through the solutions until the chloroform had completely evaporated and the resulting precipitated solids were apparently dry. Nitrogen gas was then used to purge (~1-3 mins.) residual gas vapors from the vial and the powdered samples were subsequently analyzed by <sup>1</sup>H NMR spectroscopy. The spectra were obtained in CDCl<sub>3</sub> or acetone- $\delta_6$ , as indicated. The powdered samples were again analyzed after 7 days of standing in open containers under ambient, room temperature conditions. For select gases, at least three trials were carried out in order to estimate errors. The spectra are denoted as Day 0 or Day 7 “bubbling to dryness experiments” for a variety of gases and are shown in the Synthesis and Characterization section.
- 2) **Atmospheric Pressure Method.** The gas of interest is bubbled into a saturated CHCl<sub>3</sub> solution of **Me,H,SiMe<sub>2</sub>** (~0.10 M, 1-2 mL) in a borosilicate glass vial until a precipitate starts to form. The vial is then capped, warmed slightly to re-dissolve the precipitate, and set aside to allow crystals to form, which usually occurs on a timescale of several minutes to days. Crystals generally appeared after the solutions had reached room temperature.
- 3) **General Pressure Method.** CAUTION! Contents under pressure.  
In this method, a volume of cold, liquefied gas (or a pre-weighed solid in the case of CO<sub>2</sub>) and a glass vial containing 1.0 mL of a saturated (~0.10 M) CHCl<sub>3</sub> solution of **Me,H,SiMe<sub>2</sub>** and activated 3 Å molecular sieves are placed into a cooled (liquid N<sub>2</sub>) teflon sample holder of a stainless steel digestion bomb (Parr brand, Model #4749, 23 mL total volume). The system is then quickly sealed in the digestion bomb and allowed to warm to room temperature and equilibrate over a period of days, the pressure of the gas inducing precipitation of the gas clathrate. After some days, the bomb is opened and the crystals of  $x(\text{gas})@ \text{Me,H,SiMe}_2$  are removed by filtration. During the preparation, the teflon sample holder is cooled with its cap on so as to minimize condensation of water inside the vessel.

The gas pressures achieved in this way were not measured directly, but the amount of liquefied gas was chosen so as to achieve, at a maximum, some pressure in the bomb, given the known (~20 mL) remaining free volume available in the bomb and neglecting for the solubility of the gas in the solvent. Thus, the estimated maximum possible pressure ( $P_{\text{max(est.)}}$ ) can be calculated. The actual pressure during crystal growth is therefore an undetermined (and not necessarily constant) value that is likely considerably less than  $P_{\text{max(est.)}}$ , due to gas loss during closure of the system, slow boil off of the gas during sample warming, slow dissolution into the CHCl<sub>3</sub>, and capture of the gas by the precipitating  $x(\text{gas})@ \text{Me,H,SiMe}_2$  complex. With some exceptions, most samples prepared in this way were generally consistent with respect to gas occupancy estimates from crystal to crystal (usually within 0.05 equivalents as measured by SCXRD), and the single crystal occupancies were also generally in good agreement with the bulk sample occupancies (as estimated by TGA). The consistency of gas occupancies between different batch preparations using this method, however, tended to be lower due to difficulties in accurately reproducing the volume of the cold, liquefied gas.

Notably, a batch of  $x(\text{Xe})@ \text{Me,H,SiMe}_2$  ( $x = 0.77(3)$ ,  $0.79(2)$ , for two separate single crystals isolated from this batch) prepared by this method using 3.0 mL of Xe, corresponding to an estimated maximum possible pressure,  $P_{\text{max(est.)}}$ , of 51 bar, exhibited Xe occupancies very

similar (0.79(2) equivalents of Xe, established by two separate SCXRD determinations and two TGA analyses [using the DSC pan technique]) to single crystals and bulk powder isolated from the same solution, using the “Defined Pressure method” (below) and a well-defined pressure of 9.8 bar of Xe. The observation strongly suggests that attempts to seal 3.0 mL of xenon in the Parr bomb via the “General Pressure Method” resulted in a system with an equilibrium pressure of between 9 and 10 bar, only about 20% of the  $P_{\text{max(est.)}}$ .

4) **Defined Pressure Method.** CAUTION! Contents under pressure.

Certain gas clathrate samples were grown similarly to the “General Pressure Method” above, but instead of generating gas pressure by sealing liquefied gases in the Parr bomb and allowing it to equilibrate at room temperature, a custom made stainless steel pressure vessel was used. The sample vessel, fitted with a pressure gauge and a gas valve, could be charged to and held at a constant specific gas pressure using a pressure-regulated commercial cylinder of the gas. Thus, the clathrates were grown from saturated, room temperature  $\text{CHCl}_3$  solutions ( $\sim 0.10$  M) of **Me,H,SiMe<sub>2</sub>** in the presence of activated 3 Å molecular sieves, but under well-defined and constant gas pressures as indicated.

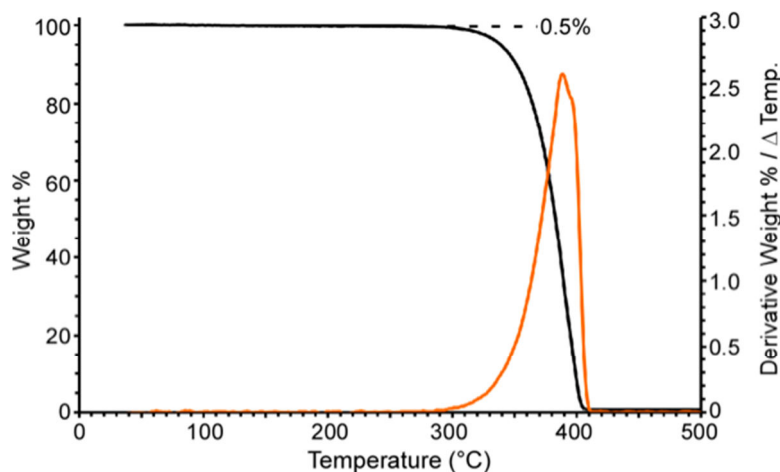
***xH<sub>2</sub>O@Me,H,SiMe<sub>2</sub>***

**Me,H,SiMe<sub>2</sub>** scavenges water, crystalizing as partial occupancy hydrates of when crystallized in open air from chloroform or ethyl acetate. A single crystal of the partial hydrate  $0.20(2)\text{H}_2\text{O}@\text{Me,H,SiMe}_2$  ( $1.6 \times 1.5 \times 0.96$  mm) was obtained by slow evaporation, in open air, of **Me,H,SiMe<sub>2</sub>** from undried chloroform. Refinement of the SCXRD data showed a residual peak of  $1.79 \text{ e}^-/\text{\AA}^3$  located in the center cavity that was modeled as a partial occupancy  $\text{H}_2\text{O}$  oxygen atom, the oxygen refining to an occupancy of 0.21. Modeling and refinement of the water oxygen atom improved  $R_1$  from 0.0519 to 0.0473. Electron density (SQUEEZE) analysis estimates  $1.75 \text{ e}^-$  per cavitand cavity (0.18 eq.  $\text{H}_2\text{O}$ ). Notably, this partial hydrate structure is different from the previously reported crystal structure of the “monohydrate” of **Me,H,SiMe<sub>2</sub>**<sup>S3</sup> in the sense that the earlier reported, room temperature structure is of low quality ( $R_1 = 9.17\%$ ), is reportedly crystallized from  $\text{CH}_2\text{Cl}_2$ —which, in our hands, gives the  $0.85(1)\text{CH}_2\text{Cl}_2$  solvate—and the reported structure models two oxygen atom sites within the cavity of the **Me,H,SiMe<sub>2</sub>** host, one of which at least exhibits very large thermal parameters.

The  $0.21(2)\text{H}_2\text{O}@\text{Me,H,SiMe}_2$  crystal ( $1.6 \times 1.5 \times 0.96$  mm) was subsequently dehydrated in an oven at  $150^\circ\text{C}$  for 1 week in a single-crystal-to-single-crystal fashion. A second data collection was performed on the crystal ( $1.6 \times 1.5 \times 0.96$  mm), which no longer showed an electron density peak in the center of the cavity. The largest residual peak in the difference Fourier map was  $0.25 \text{ e}^-/\text{\AA}^3$  and was significantly offset from the center of the cavity, demonstrating that the cavities are empty. SQUEEZE analysis of this data estimated  $1.63 \text{ e}^-$  per cavitand cavity, illustrating the limitations of the SQUEEZE procedure for estimating small amounts of electron density. Lastly, the empty single crystal of **Me,H,SiMe<sub>2</sub>** ( $1.6 \times 1.5 \times 0.96$  mm) obtained above was placed in a humidity chamber at room temperature for approximately 24 days, after which time a third data set was collected at 100 K. Structure solution and refinement revealed that the crystal had taken up, on average, approximately 0.29(2) equivalents of water,  $0.29(2)\text{H}_2\text{O}@\text{Me,H,SiMe}_2$ . A clear electron density peak attributable to the oxygen of a water molecule was observed in the center of the cavity and refined to 0.28 oxygen; SQUEEZE analysis estimated this data estimated  $3 \text{ e}^-$  per cavitand cavity. Notably, the crystal showed an improvement in diffraction quality upon  $\text{H}_2\text{O}$  loss via heating and subsequent uptake, as evidenced by the percent of observed reflection intensities for the three data sets (70%, 76%, and 81% to  $2\theta = 50^\circ$  for  $0.20(2)\text{H}_2\text{O}@\text{Me,H,SiMe}_2$ , empty **Me,H,SiMe<sub>2</sub>**, and  $0.29(2)\text{H}_2\text{O}@\text{Me,H,SiMe}_2$ , respectively). The

improvement in crystal diffraction quality may be a result of annealing effects.

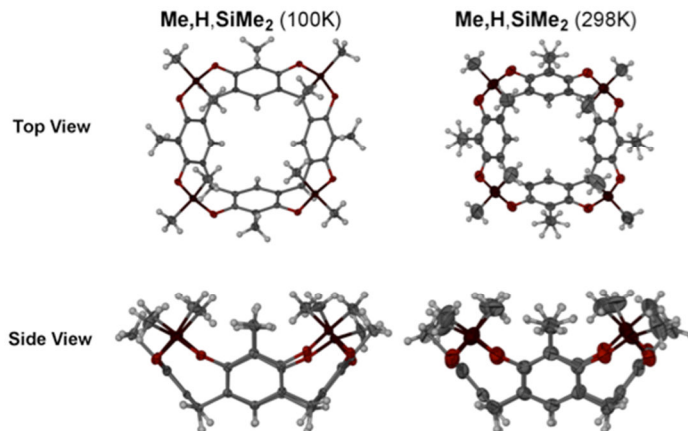
A room temperature collection was obtained on a second empty crystal that was prepared from the partial hydrate in the same manner as described above. Summary crystallographic data are provided in Table S4. It should be noted that slow evaporation of **Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** from wet solution of THF and acetone gave partial water occupancy hydrates of 0.24 and 0.38 eq., respectively.



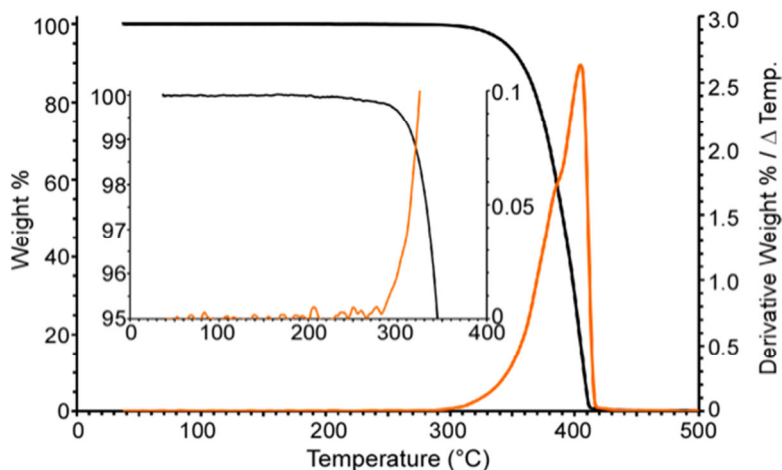
**Supporting Figure S6.** TGA [open pan] of  $x(\text{H}_2\text{O})@\text{Me}_2\text{H}_2\text{SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). The 0.5% mass loss equates to 0.21 equivalents of  $\text{H}_2\text{O}$ .

### Empty **Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>**

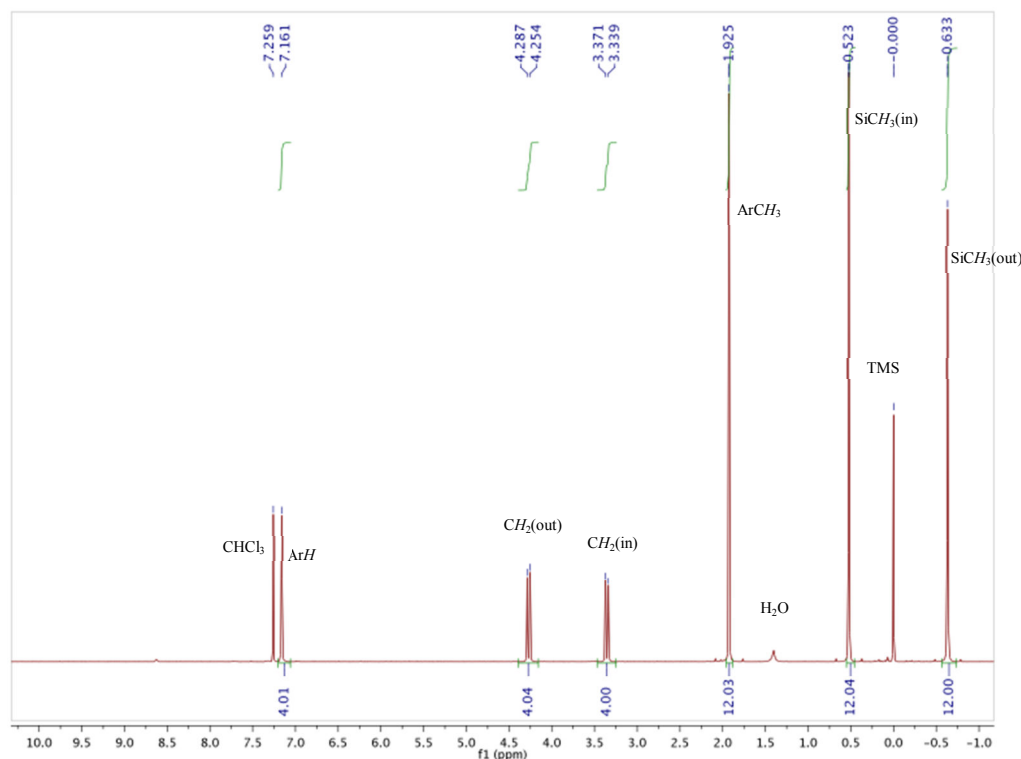
Generation of empty **Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** was carried out by taking the bulk solid of  $x(\text{H}_2\text{O})@\text{Me}_2\text{H}_2\text{SiMe}_2$  (isolated from reaction workup and purification) and heating at 150°C for at least 2 days. Single crystals of  $x(\text{H}_2\text{O})@\text{Me}_2\text{H}_2\text{SiMe}_2$  were similarly treated and were similarly emptied in a single-crystal-to-single-crystal fashion. A summary of the SCXRD data can be found in Supporting Table S4. TGA data showing sublimation of pure, empty **Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** shows no noticeable mass loss up to 300 °C.



**Supporting Figure S7.** Thermal ellipsoid plots of **Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** collected at 100 K and 298 K at the 50% probability level (gray – carbon, red – oxygen, maroon – silicon, white – hydrogen).



**Supporting Figure S8.** TGA of empty **Me,H,SiMe<sub>2</sub>** (black). The derivative curve is depicted in orange. Inset: magnified view.



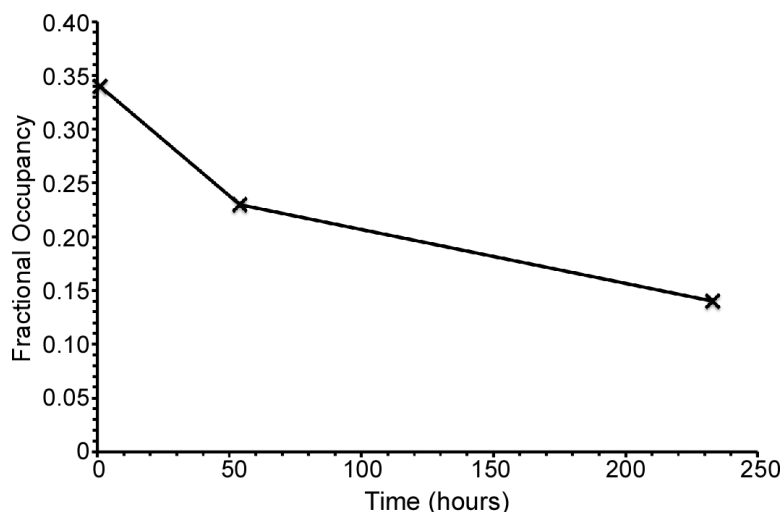
**Supporting Figure S9.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of pure, empty **Me,H,SiMe<sub>2</sub>**. The water peak at about 1.5 ppm is due to wet CDCl<sub>3</sub>.

### **0.34(N<sub>2</sub>)@Me,H,SiMe<sub>2</sub>**

Single crystals of a dinitrogen clathrate were prepared by the Defined Pressure Method (above) using a customized stainless steel bomb held at a fixed, 80 bar pressure of ultrahigh purity N<sub>2</sub>. The bomb was opened and the precipitated crystals of *x*(N<sub>2</sub>)@**Me,H,SiMe<sub>2</sub>** were removed by filtration. One single crystal from the batch (0.37×0.21×0.13 mm) was quickly mounted on the diffractometer at 100 K and its structure determined. The bulk sample was subjected to TGA analysis within one hour of

isolation. The remaining material was stored in a desiccator at room temperature. The composition of the analyzed single crystal was found to be  $0.34(2)\text{N}_2@\text{Me}_3\text{H}_2\text{SiMe}_2$  according to SHELXL refinement and SQUEEZE treatment of the data. After refinement of the host moiety, the two highest peaks in the difference electron density map appear approximately in the center cavity ( $2.23$  and  $1.93\text{ e}^-/\text{\AA}^3$ ), being clearly attributable to a partial occupancy molecule of  $\text{N}_2$ . Modeling and refinement of the  $\text{N}_2$  species improved the absolute  $R_1$  value by  $\sim 1.3\%$ . Alternative refinements (*e.g.* as a partial occupancy  $\text{H}_2\text{O}$ ) gave significantly more disagreeable refinements. The anisotropic displacement parameters of the  $\text{N}_2$  species are somewhat large, but reasonable, indicating an ordered, but librational distorted  $\text{N}_2$  species. The refined  $\text{N}_2$  bond length of  $0.918(12)\text{ \AA}$  is considerably shorter than the experimentally accepted value of  $1.098\text{ \AA}$ , likely due to librational effects. TGA analysis of this sample (after extended furnace purging) shows a mass loss of  $\sim 0.7\%$ , which equates to  $0.20$  equivalents of  $\text{N}_2$ . Tandem TGA-MS analysis of the complex did not conclusively demonstrate the release of  $\text{N}_2$  by mass spectrometry due to the presence of residual nitrogen from air in the furnace, even after purging the furnace for 8 hours with He carrier gas.

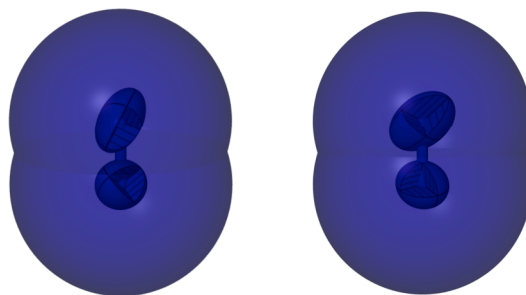
A second, higher quality, crystal of the  $x(\text{N}_2)@\text{Me}_3\text{H}_2\text{SiMe}_2$  batch sample ( $0.90\times 0.26\times 0.08\text{ mm}$ ) was analyzed, but after the crystals had been isolated and stored at room temperature, in a desiccator, for 54 hours. Refinement of the data from this crystal proceeded similarly to the first crystal, though the refined  $\text{N}_2$  occupancy was lower, measuring  $0.23(2)\text{N}_2@\text{Me}_3\text{H}_2\text{SiMe}_2$  likely due to partial  $\text{N}_2$  loss during the 54 hour storage period. The  $\text{N}_2$  bond length in this crystal refined to be  $0.923(15)\text{ \AA}$ , somewhat consistent with the first structure determination. Immediately following the low temperature data collection, the second crystal was returned to the desiccator and stored at room temperature for another 179 hours ( $233\text{ hours}-9\text{ days}, 17\text{ hours}$ —total time at room temperature), after which another data collection was obtained at  $100\text{ K}$ . The composition of the crystal at this time refined to be  $0.14(5)\text{N}_2@\text{Me}_3\text{H}_2\text{SiMe}_2$ ; the  $\text{N}_2$  was refined with isotropic displacement parameters and the bond length measured  $0.98(3)\text{ \AA}$ . Notably, the crystal showed no deterioration in diffraction quality upon  $\text{N}_2$  loss as evidenced by the percent of observed reflection intensities under the same collection conditions ( $77.9\%$  and  $77.5\%$  to  $2\theta = 56^\circ$  for  $0.23(2)\text{N}_2@\text{Me}_3\text{H}_2\text{SiMe}_2$  and  $0.14(5)\text{N}_2@\text{Me}_3\text{H}_2\text{SiMe}_2$ , respectively). A summary of the SCXRD data can be found in Supporting Tables S4.



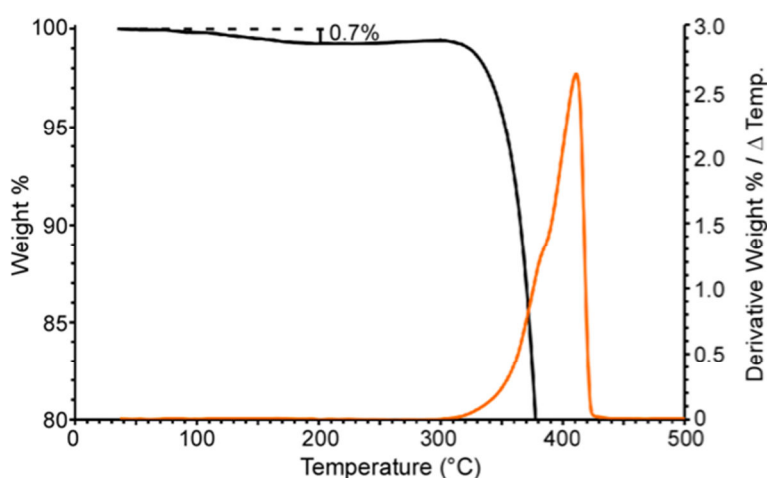
**Supporting Figure S10.** Plot of fractional occupancy versus time of a single crystal of  $x(\text{N}_2)@\text{Me}_3\text{H}_2\text{SiMe}_2$ . The time points at times 34 and 233 hours are of the same crystal (kept under ambient conditions) and the time point at 1 hour is from a separate single crystal from the same batch.

0.34(N<sub>2</sub>)@Me,H,SiMe<sub>2</sub>

0.23(N<sub>2</sub>)@Me,H,SiMe<sub>2</sub>



**Supporting Figure S11.** Thermal ellipsoid plots of the N<sub>2</sub> species in single crystals of 0.34(N<sub>2</sub>)@Me,H,SiMe<sub>2</sub> and 0.23(N<sub>2</sub>)@Me,H,SiMe<sub>2</sub> (2<sup>nd</sup> crystal).

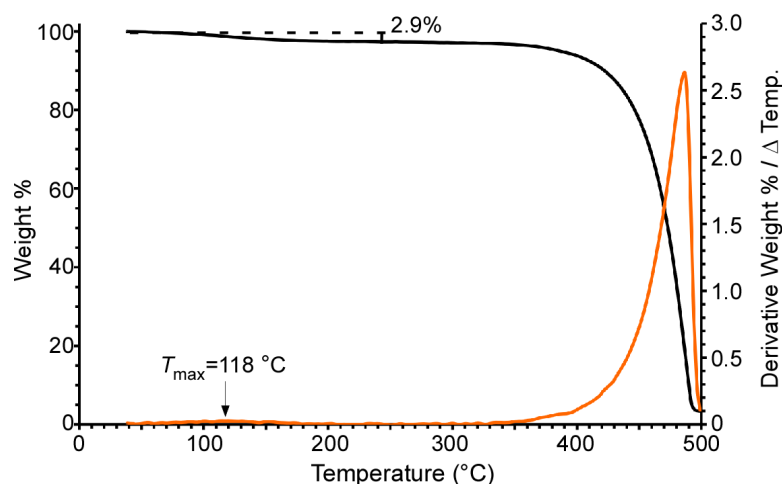


**Supporting Figure S12.** TGA [open pan] of 0.34(N<sub>2</sub>)@Me,H,SiMe<sub>2</sub> at Day 0 (black) and derivative weight curve (orange). A mass loss of 0.7% equates to 0.20 equivalents of N<sub>2</sub>.

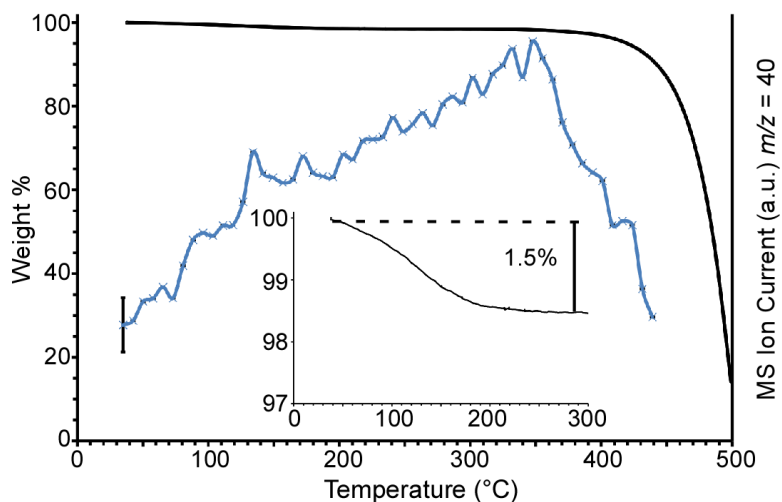
### 0.61(Ar)@Me,H,SiMe<sub>2</sub>

Single crystals of an argon clathrate were grown from chloroform at room temperature according to the Defined Pressure Method (above) using a customized stainless steel bomb held at a fixed pressure of 80 bar. One crystal was analyzed by SCXRD immediately following isolation and gave a refined composition of 0.61(4)Ar@Me,H,SiMe<sub>2</sub>. Though it is formally difficult to demonstrate from the SCXRD data alone that the sample is not a partial hydrate, importantly, the observed the electron density within the cavity (peak height, refined occupancy, SQUEEZE electron density) was far greater than for any hydrate crystals isolated to date, and also greater than one oxygen atom (1.37 oxygens). Moreover, TGA analysis of *x*(Ar)@Me,H,SiMe<sub>2</sub> crystals shows significantly different behavior from *x*(H<sub>2</sub>O)@Me,H,SiMe<sub>2</sub> in the sense that freshly prepared 0.61(Ar)@Me,H,SiMe<sub>2</sub> shows a more well defined mass loss and a greater total mass loss (2.9%, equating to 0.58 equivalents or Ar) than for any sample of *x*(H<sub>2</sub>O)@Me,H,SiMe<sub>2</sub> (Figure S13). Also, TGA-MS analysis of the bulk material after three days of storage in a dessicator, which showed a 1.5% (0.29 equivalents Ar) mass loss, clearly indicates the presence of Ar through its release upon heating (Figure S14).

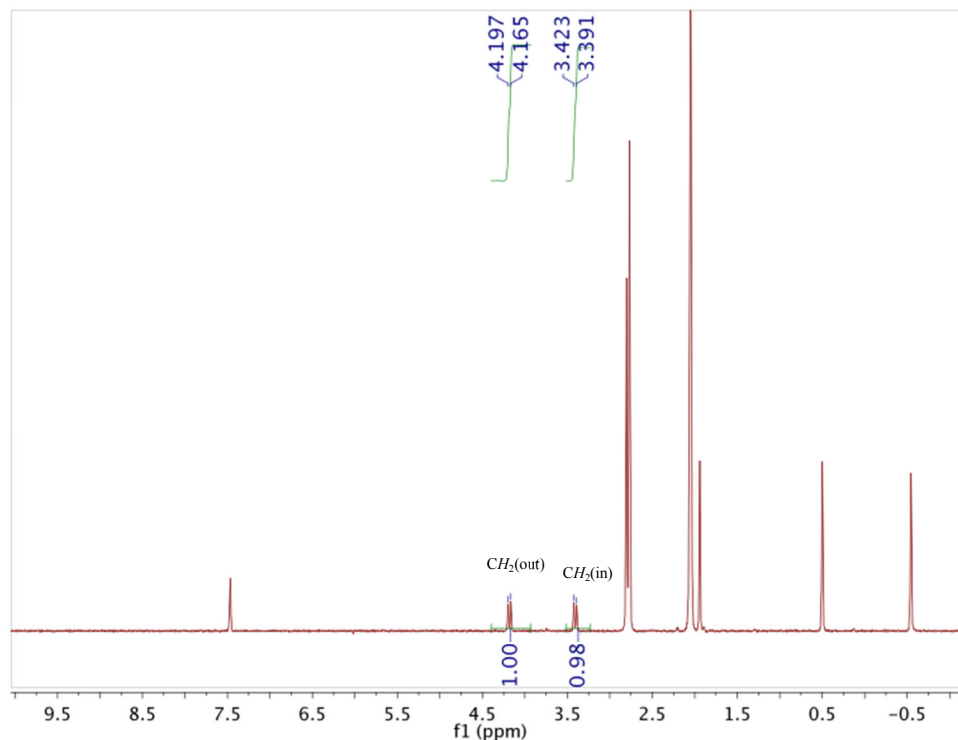




**Supporting Figure S13.** TGA [DSC pan technique] of  $0.61(\text{Ar})@ \text{Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). A 2.9% mass loss equates to 0.58 equivalents of Ar.



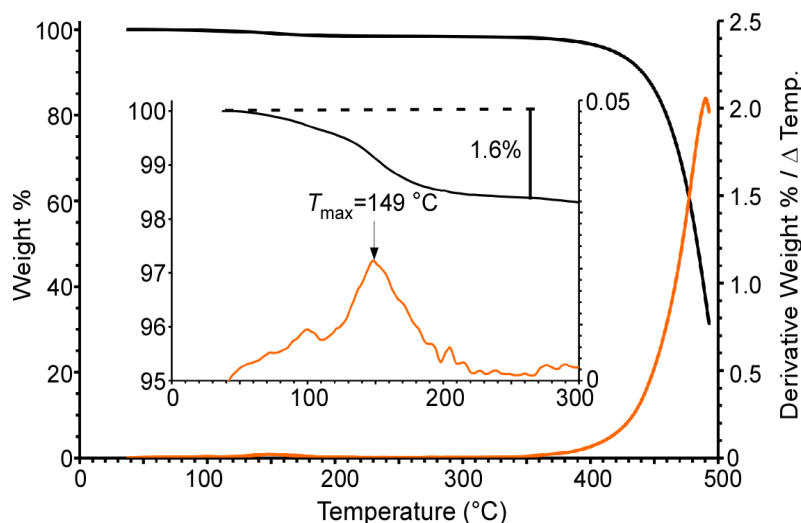
**Supporting Figure S14.** TGA-MS [open pan] analysis of a sample of  $0.61(\text{Ar})@ \text{Me,H,SiMe}_2$  that had been stored at room temperature in a desiccator for 3 days. MS ion current at  $m/z = 40$  (blue). The error bar on the first data point indicates two standard deviations of the background signal at  $m/z = 40$  for the thirty minutes prior to heating the sample. Inset: magnified view. A 1.5% mass loss equates to 0.29 equivalents of Ar.



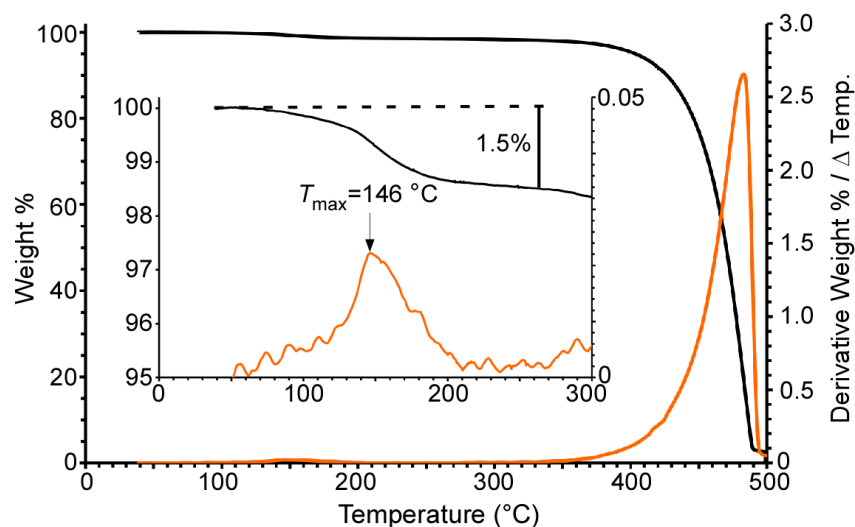
**Supporting Figure S15.**  $^1\text{H}$  NMR spectrum ( $\text{acetone-}d_6$ ) of  $x(\text{Ar})@Me,H,SiMe_2$  batch crystals at Day 0. The peaks at 2.81 and 2.84 correspond to residual water in the solvent.

#### $x(\text{CH}_4)@Me,H,SiMe_2$

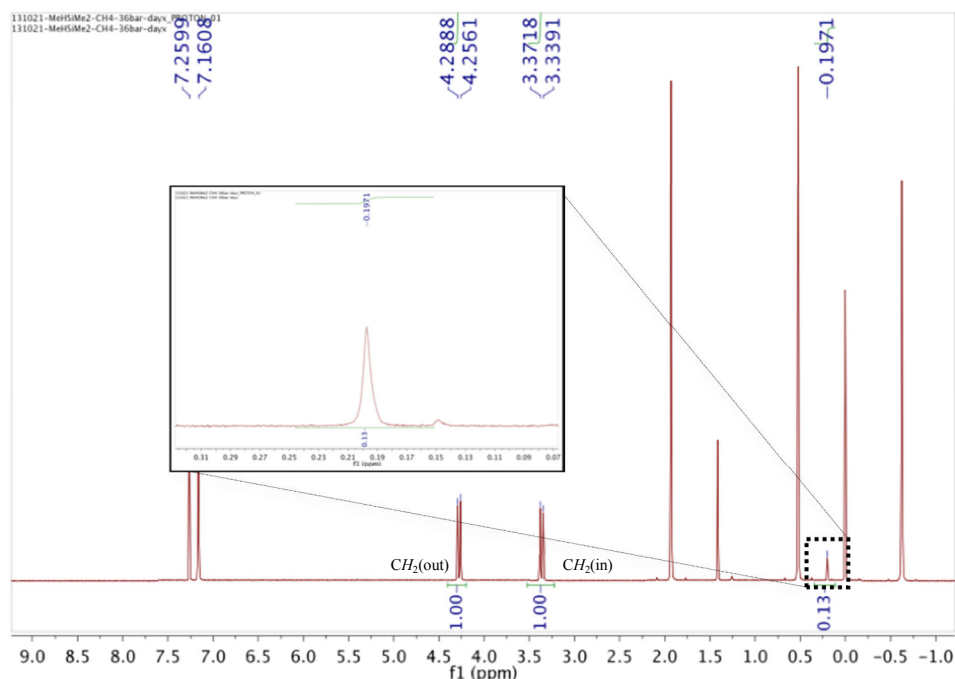
Single crystals of a methane clathrate were grown from chloroform at room temperature according to the Defined Pressure Method (above) using a customized stainless steel bomb held at a fixed pressure of 36 bar. This gave crystals that were analyzed by SCXRD, TGA and  $^1\text{H}$  NMR spectroscopy. Refinement of the SCXRD data revealed a peak of  $5.6 \text{ e}^-/\text{\AA}^3$  within the cavity. The peak was modeled as a carbon atom with a refined occupancy of 0.83 (Table S4). SQUEEZE analysis of this data estimates  $7.4 \text{ e}^-$  per cavitand cavity (0.74 eq.  $\text{CH}_4$ ). Thus, the crystal composition is estimated as  $0.79(6)\text{CH}_4@Me,H,SiMe_2$ . Though it is formally difficult to demonstrate from the SCXRD data alone that the sample is not a partial hydrate, importantly, the observed the electron density within the cavity (peak height, refined occupancy, SQUEEZE electron density) was far greater than for any hydrate crystals isolated to date, equating to  $\sim 0.74$  water molecules, supporting the guest assignment as methane.  $^1\text{H}$  NMR analysis of the crystals shows at least 0.13 eq. of methane per cavitand (Figure S18). The differences in occupancies between SCXRD and  $^1\text{H}$  NMR may be due to the low solubility of methane in  $\text{CDCl}_3$  and gas rapidly escaping the solvent upon dissolution of the clathrate. TGA data shows 1.6% weight loss up to  $240^\circ\text{C}$  (Figure S16), which corresponds to 0.78 equivalents of methane, consistent with the SCXRD estimated occupancy. After 5 days at room temperature in a desiccator, TGA shows that there has been almost no loss of methane; the observed weight loss of 1.5% corresponding to 0.73 eq. of methane. Similarly, the original single crystal of  $0.79(6)\text{CH}_4@Me,H,SiMe_2$  was re-analyzed by SCXRD after 5 days of storage at room temperature in a desiccator, the data giving an estimated composition of  $0.84(8)\text{CH}_4@Me,H,SiMe_2$  (TGA in Figure S17). Notably, the crystal showed almost no deterioration in diffraction quality upon storage, as evidenced by the percent of observed reflection intensities (81% and 82% to  $2\theta = 50^\circ$  for the original 8 seconds/degree exposure and for the second, 10 seconds/degree exposure, respectively).



**Supporting Figure S16.** TGA [DSC pan technique] of  $0.79(\text{CH}_4)@\text{Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). Inset shows zoomed in region showing guest loss. The 1.6% mass loss equates to 0.78 equivalents of  $\text{CH}_4$ .



**Supporting Figure S17.** TGA [DSC pan technique] of  $0.79(\text{CH}_4)@\text{Me,H,SiMe}_2$  at Day 5 (black) and derivative weight curve (orange). Inset shows zoomed in region showing guest loss. The 1.5% mass loss equates to 0.73 equivalents of  $\text{CH}_4$ .

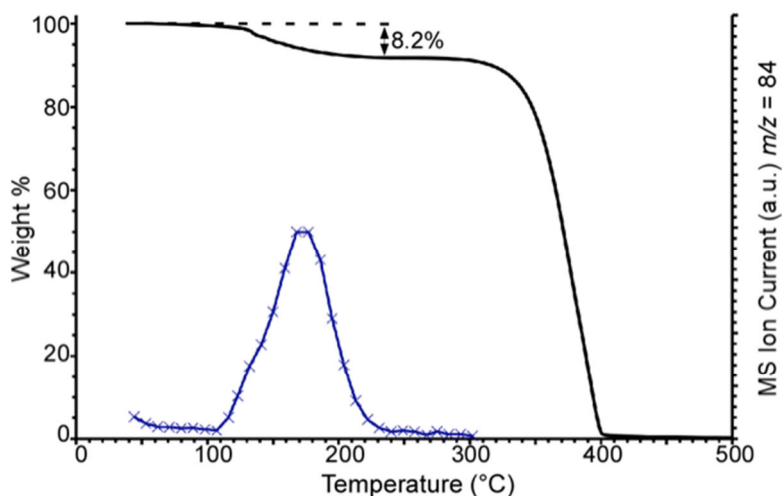


**Supporting Figure S18.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of  $0.79(\text{CH}_4)@\text{Me,H,SiMe}_2$  batch crystals at Day 0. Inset: Magnified view of methane signal. The integrated area corresponds to 0.13 equivalents of methane.

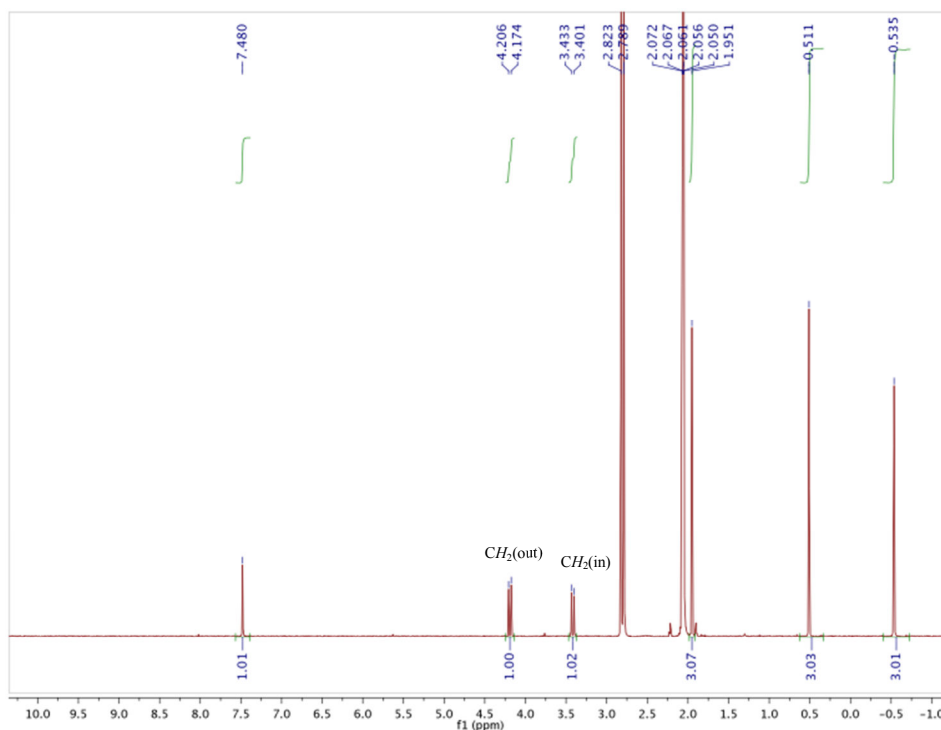
### $x(\text{Kr})@\text{Me,H,SiMe}_2$

Crystals of a krypton clathrate were grown from  $\text{CHCl}_3$  at room temperature by the General Pressure Method (above) using 3.0 mL of Kr ( $P_{\text{max(est.)}} \ll 70$  bar). This gave a single crystal with a composition of  $0.51(3)\text{Kr}@\text{Me,H,SiMe}_2$  ( $0.49 \times 0.14 \times 0.11$  mm), as determined by SCXRD analysis. The  $0.51(3)\text{Kr}@\text{Me,H,SiMe}_2$  crystal ( $0.49 \times 0.14 \times 0.11$  mm) was then heated at  $100^\circ\text{C}$  for two weeks and a subsequent SCXRD data collection and refinement showed a peak of  $4.44 \text{ e}^-/\text{\AA}^3$  centered in the cavity, refining to  $0.07(1)$  equivalents of residual krypton. Notably, the crystal showed almost no deterioration in diffraction quality upon Kr loss, as evidenced by the percent of observed reflection intensities (69% and 67% to  $2\theta = 56^\circ$  for  $0.51(3)\text{Kr}@\text{Me,H,SiMe}_2$  and  $0.07(1)\text{Kr}@\text{Me,H,SiMe}_2$ , respectively). The magnitude of the electron density ( $> 0.5$  oxygen) and its position ( $d = 0.43 \text{ \AA}$ ) in the cavity allows the unambiguous conclusion that the electron density found with the cavitated cavities after heating of the crystal corresponds to residual krypton, as opposed to other conceivable assignments (*e.g.*, a water molecule: where the maximum occupancy observed occupancy is about  $0.38 \text{ eq.}$ , and  $d = 0.30(2) \text{ \AA}$ ).

The original bulk sample was analyzed numerous times by TGA, using open TGA pans, and generally gave inconsistent results that always indicated a greater than anticipated amount (based on SCXRD) of enclathrated krypton due to Kr loss inducing some co-sublimation of the  $\text{Me,H,SiMe}_2$  (Figure S19). The bulk sample was analyzed by TGA-MS (below) after 7 days storage under ambient conditions and showed clearly the release of Kr ( $m/z = 84$  amu) concomitant with the mass loss.  $^1\text{H}$  NMR of the fresh sample shows no proton containing impurities (Figure S20).



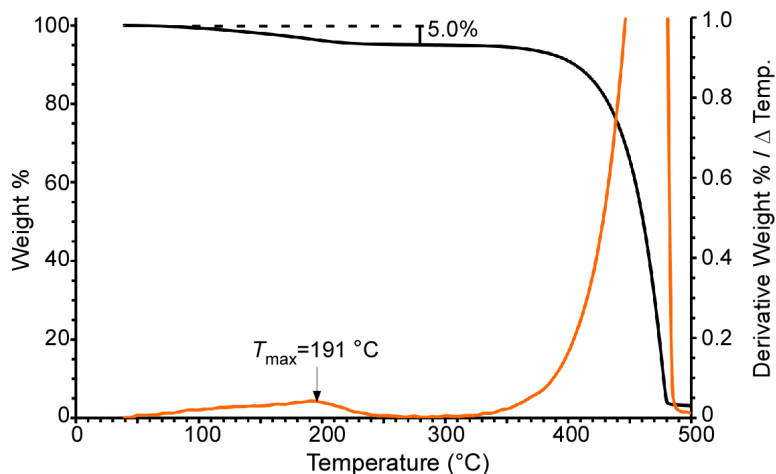
**Supporting Figure S19.** TGA-MS [open pan] of a sample of  $0.51\text{Kr}@Me,H,SiMe_2$  after 7 days storage at room temperature (black). MS ion current at  $m/z = 84$  (blue). An 8.2% mass loss equates to 0.84 equivalents of krypton, a value that is artificially high due to induced co-sublimation of  $Me,H,SiMe_2$ . Similarly, the  $T_{\text{max}}$  value is artificially low due to co-sublimation of  $Me,H,SiMe_2$ .



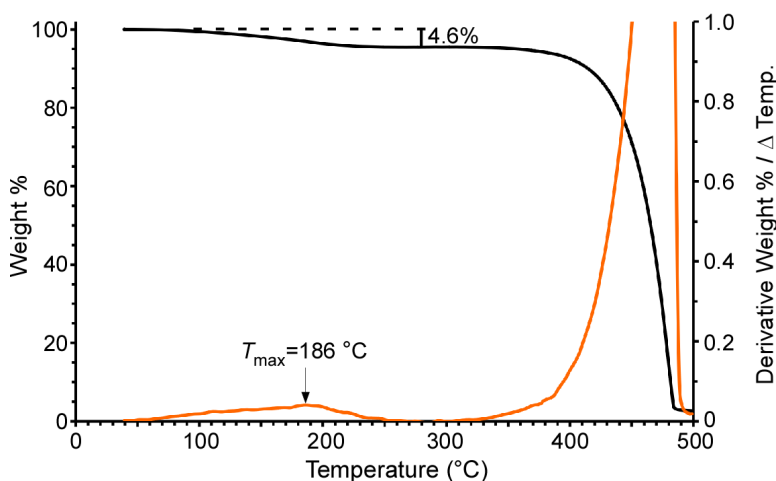
**Supporting Figure S20.**  $^1\text{H}$  NMR spectrum (acetone- $\delta_6$ ) of  $x(\text{Kr})@Me,H,SiMe_2$  batch crystals at Day 0 showing no protic impurities.

Single crystals of  $x\text{Kr}@Me,H,SiMe_2$  were also grown from chloroform at room temperature according to the Defined Pressure Method (above) using a customized stainless steel bomb held at a fixed pressure of 9.8 bar. A single crystal with an estimated composition of  $0.52(1)\text{Kr}@Me,H,SiMe_2$  ( $0.52 \times 0.20 \times 0.19$

mm) was isolated. TGA analysis of the bulk sample on the day of isolation, using punctured DSC pans, gave a reproducible mass loss of 5.0%, corresponding to loss of 0.48 equivalents of krypton (Figure S21). TGA analysis of the same sample, after storage of the sample for 3 days at room temperature in a desiccator, showed a 4.6% mass loss, corresponding to 0.44 equivalents of krypton (Figure S22).



**Supporting Figure S21.** TGA [DSC pan technique] of  $0.50(\text{Kr})@ \text{Me,H,SiMe}_2$  (black) and derivative weight curve (orange). A 5.0% mass loss equates to 0.48 equivalents of krypton.

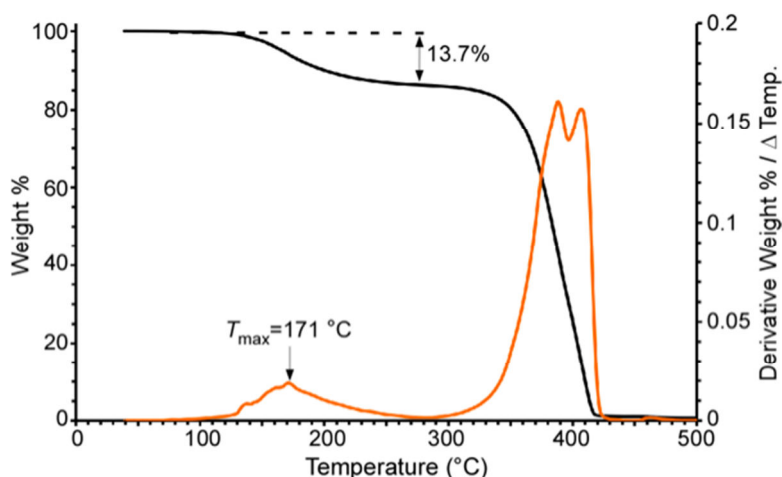


**Supporting Figure S22.** TGA [DSC pan technique] of a sample of  $0.50(\text{Kr})@ \text{Me,H,SiMe}_2$  (black) after 3 days storage at room temperature. Derivative weight curve (orange). A 4.6% mass loss equates to 0.44 equivalents of krypton.

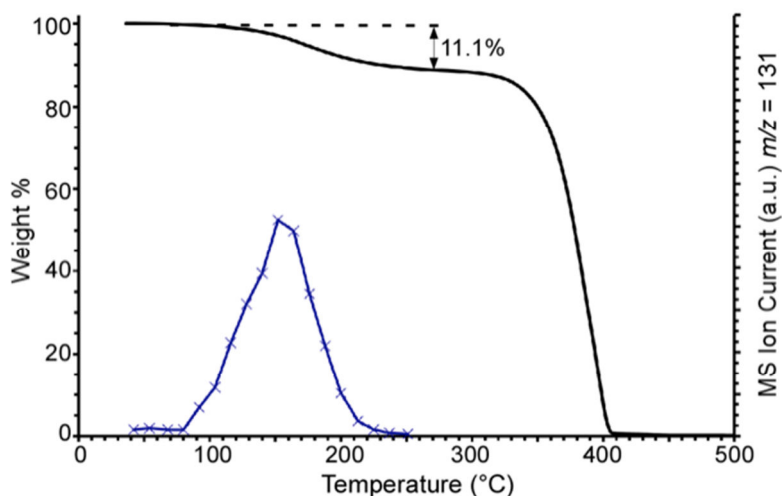
### $x(\text{Xe})@ \text{Me,H,SiMe}_2$

Crystals of a xenon clathrate were precipitated from  $\text{CHCl}_3$  at room temperature by the General Pressure Method (above) using 3.0 mL of Xe (solidified) ( $P_{\text{max(est.)}} \ll 51$  bar). This gave single crystals of  $0.77(3)\text{Xe}@ \text{Me,H,SiMe}_2$  that were analyzed by SCXRD upon isolation. Another crystal from the same batch preparation was analyzed after 112 days storage under ambient room temperature conditions, giving a refined composition of  $0.79(2)\text{Xe}@ \text{Me,H,SiMe}_2$ . The original bulk sample was analyzed numerous times by TGA and, using open pans, generally gave inconsistent results that all indicated a greater than expected amount of enclathrated xenon due to co-sublimation of the host concomitant with Xe loss (Figure S23). The bulk sample was

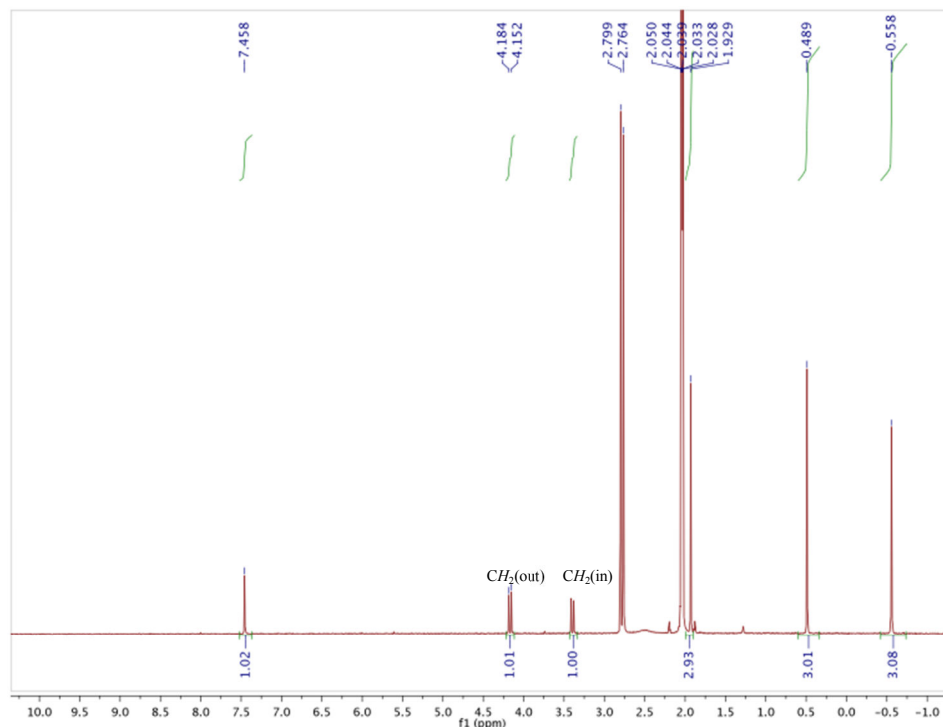
analyzed by TGA-MS after 7 days under ambient conditions and showed clearly the release of Xe ( $m/z = 131$  amu) concomitant with mass loss (Figure S24).  $^1\text{H}$  NMR analysis of the sample at Day 0 shows no proton containing impurities (Figure S25).



**Supporting Figure S23.** TGA [open pan] of 0.77(Xe)@Me,H,SiMe<sub>2</sub> at Day 0 (black) and derivative weight curve (orange). The 13.7% mass loss (equating to 0.94 equivalents of xenon) was not reproducible using open TGA pans.

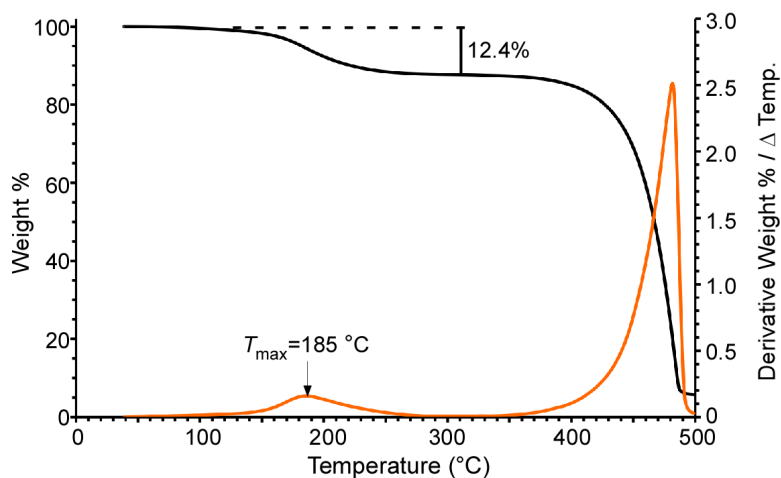


**Supporting Figure S24.** TGA-MS [open pan] of  $x(\text{Xe})@ \text{Me,H,SiMe}_2$  after room temperature storage of 0.77(Xe)@Me,H,SiMe<sub>2</sub> for 7 days (black) with the MS ion current at  $m/z = 131$  (blue) indicating xenon loss. An 11.1% mass loss equates to 0.76 equivalents of xenon, though this value was not generally reproducible using open TGA pans.



**Supporting Figure S25.**  $^1\text{H}$  NMR spectrum (acetone- $\delta_6$ ) of  $0.77(3)\text{Xe@Me,H,SiMe}_2$  batch crystals at Day 0 showing no protic impurities.

Single crystals of  $x\text{Xe@Me,H,SiMe}_2$  were also grown from chloroform at room temperature according to the Defined Pressure Method (above) using a customized stainless steel bomb held at a fixed pressure of 9.8 bar. TGA analysis of the bulk sample, using punctured DSC pans, gave a reproducible mass loss of 12.4%, corresponding to loss of 0.83 equivalents of xenon (Figure S26). A single crystal ( $0.42 \times 0.21 \times 0.21$  mm) was isolated and its structure was determined by SCXRD, giving a refined composition of  $0.79(2)\text{Xe@Me,H,SiMe}_2$ .

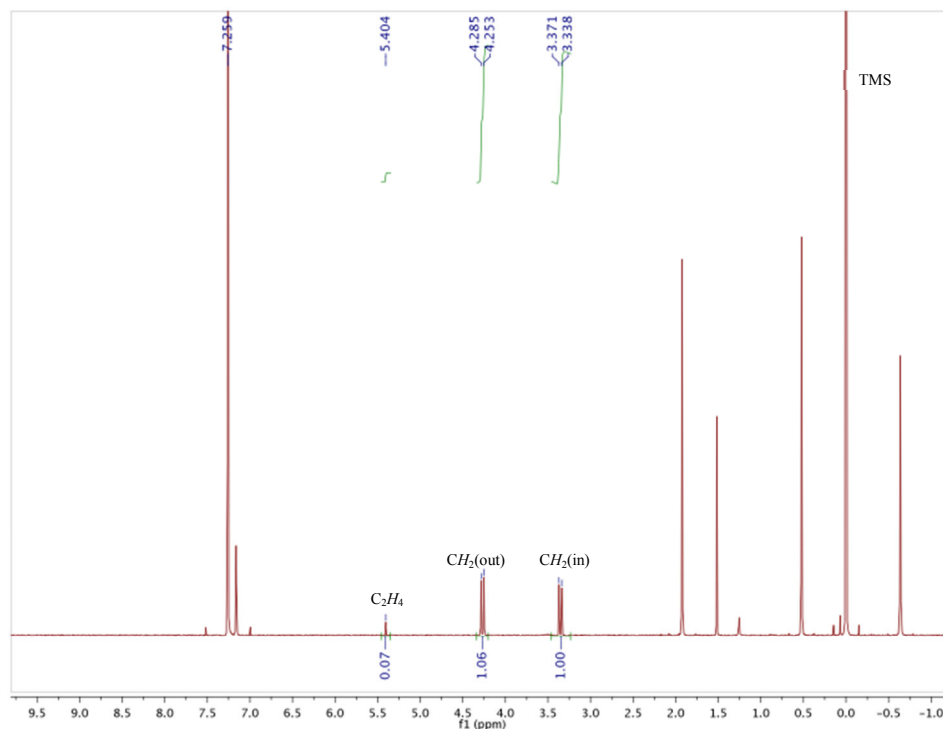


**Supporting Figure S26.** TGA [DSC pan technique] of  $0.79(\text{Xe})\text{@Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). The 12.4% mass loss equates to 0.83 equivalents of xenon.

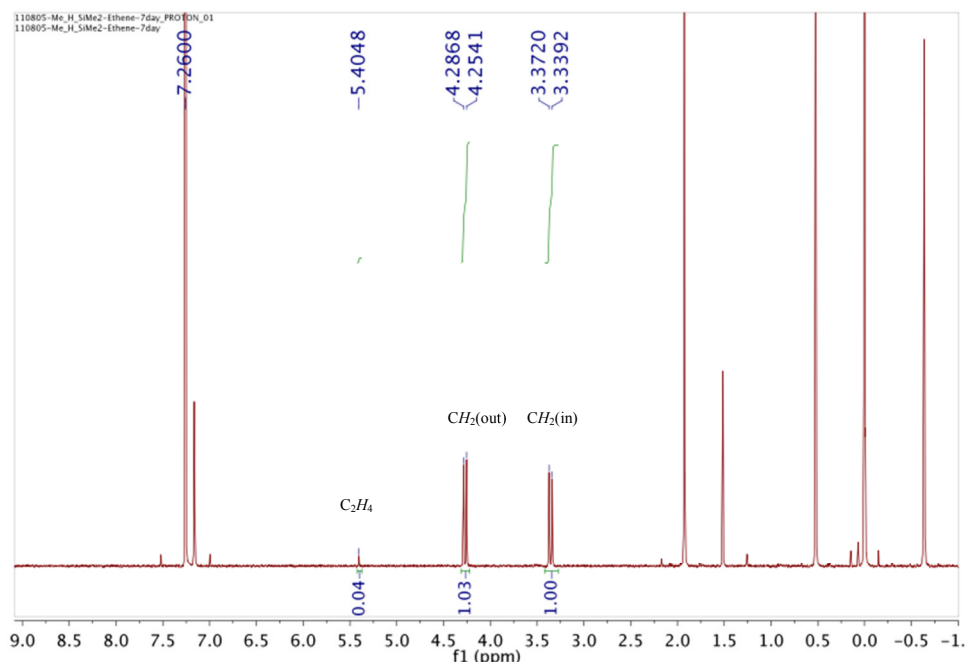


**$x(\text{C}_2\text{H}_4)@ \text{Me,H,SiMe}_2$**

Powdered  $x\text{CH}_2=\text{CH}_2@ \text{Me,H,SiMe}_2$  was prepared by the Bubbling to Dryness Method (above), by passing ethylene gas through a solution of **Me,H,SiMe<sub>2</sub>** until dryness. The powder was flushed with a stream of nitrogen for 1 min. and was subsequently analyzed by  $^1\text{H}$  NMR spectroscopy (Figure S27) and again seven days later (Figure S28), revealing the enclathration of at least 0.062(9) equivalents and 0.037(1) equivalents of ethylene, respectively. Though they are reproducible, the  $^1\text{H}$  NMR spectra likely underestimate the actual gas occupancy of the clathrate due to the low solubility of ethylene in  $\text{CDCl}_3$  and gas rapidly escaping the NMR solvent upon dissolution of the clathrate.



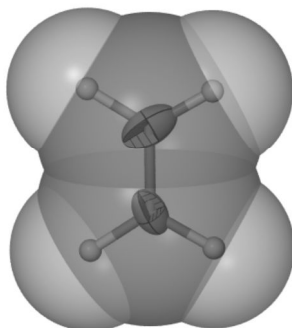
**Supporting Figure S27.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a “Bubbling to Dryness Method” preparation of  $x(\text{C}_2\text{H}_4)@ \text{Me,H,SiMe}_2$  (1 atm  $\text{C}_2\text{H}_4$ ). The integrated area of the signal at 5.4 ppm equates to 0.06 equivalents of ethylene.



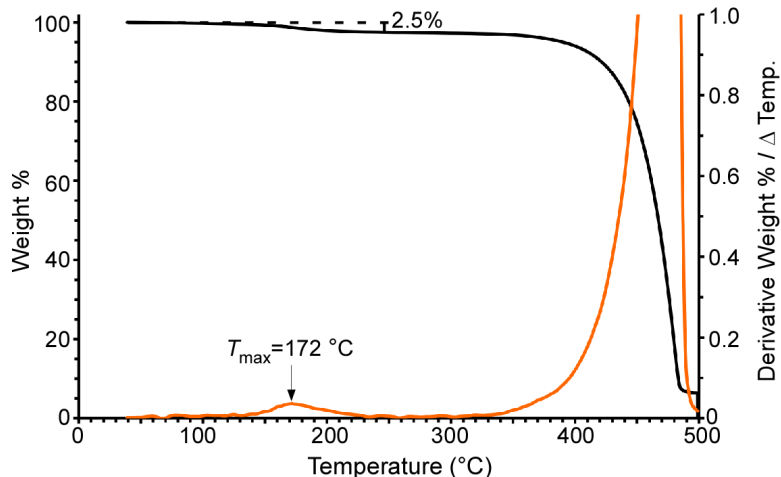
**Supporting Figure S28.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a “Bubbling to Dryness Method” preparation of  $x(\text{C}_2\text{H}_4)@\text{Me,H,SiMe}_2$  (1 atm  $\text{C}_2\text{H}_4$ ), but after 7 days of storage under ambient conditions. The integrated area of the signal at 5.4 ppm equates to 0.04 equivalents of ethylene.

Single crystals of a higher occupancy  $x(\text{C}_2\text{H}_4)@\text{Me,H,SiMe}_2$  clathrate were also grown from chloroform at room temperature according to the Defined Pressure Method (above) using a customized stainless steel bomb held at a fixed pressure of 9.8 bar. A single crystal of  $0.61(4)\text{C}_2\text{H}_4@\text{Me,H,SiMe}_2$  ( $0.66 \times 0.45 \times 0.38$  mm) was isolated and its structure was re-determined 11 days after isolation of the bulk sample at room temperature in a desiccator. The freely refined C=C bond length measured  $1.323(6)$  Å, and compares with that determined by SCRXD for crystalline ethylene at 85 K ( $1.318(5)$  Å).<sup>S9</sup> The thermal ellipsoid plot of the partial occupancy ethylene is shown below (Figure S29). TGA analysis of the bulk sample, using punctured DSC pans, gave a reproducible mass loss of 2.5%, corresponding to loss of 0.69 equivalents of ethylene (Figure S30). TGA analysis of the same sample, after storage of the sample for 4 days at room temperature, showed a 2.5% mass loss, corresponding to 0.69 equivalents of ethylene (Figure S31).

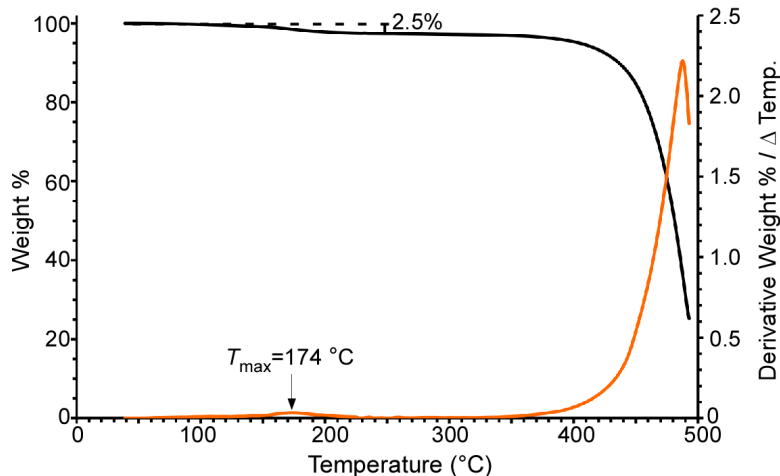
$0.61(\text{C}_2\text{H}_4)@\text{Me,H,SiMe}_2$



**Supporting Figure S29.** Thermal ellipsoid plot of the  $\text{C}_2\text{H}_4$  species in the single crystal of  $0.61(4)\text{C}_2\text{H}_4@\text{Me,H,SiMe}_2$ .

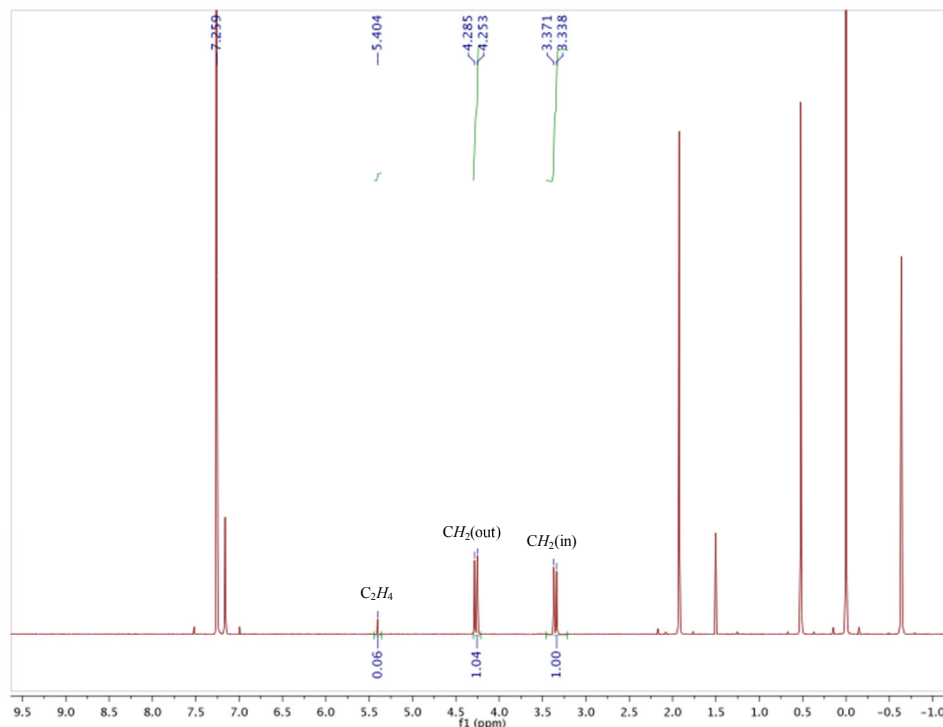


**Supporting Figure S30.** TGA [DSC pan technique] of 0.61(C<sub>2</sub>H<sub>4</sub>)@Me,H,SiMe<sub>2</sub> at Day 0 (black) and derivative weight curve (orange). A 2.5% mass loss equates to 0.69 equivalents of ethylene.

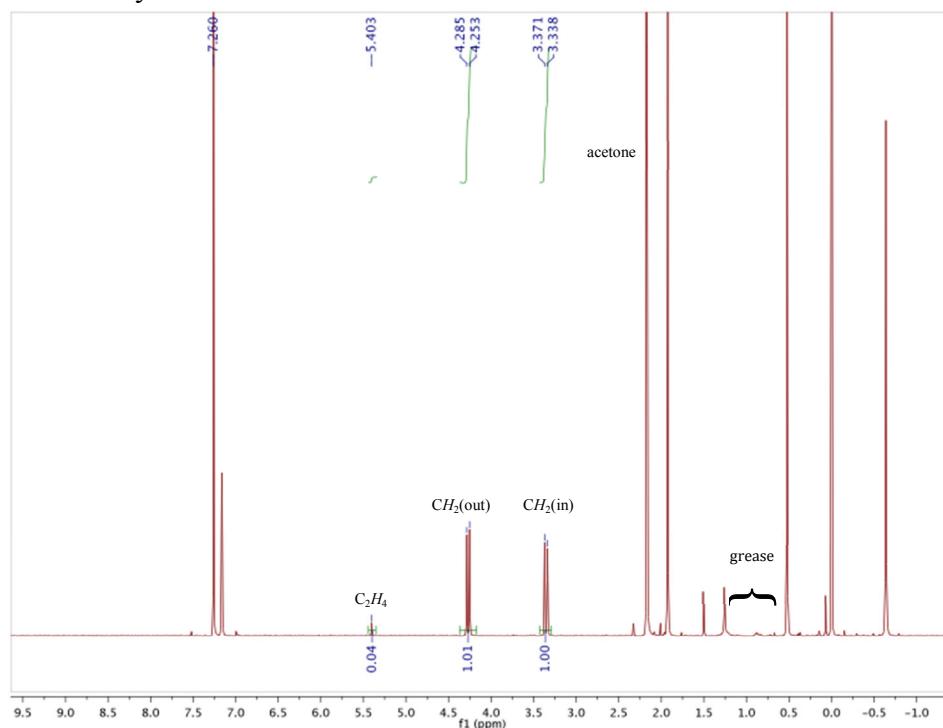


**Supporting Figure S31.** TGA [DSC pan technique] of 0.61(C<sub>2</sub>H<sub>4</sub>)@Me,H,SiMe<sub>2</sub> at Day 4 (black) and derivative weight curve (orange). A 2.5% mass loss equates to 0.69 equivalents of ethylene.

Single crystals of the ethylene clathrate were precipitated from CHCl<sub>3</sub> at room temperature by the General Pressure Method (above) using 3.0 mL of C<sub>2</sub>H<sub>4</sub> ( $P_{\text{max(est.)}} \leq 45$  bar). <sup>1</sup>H NMR spectroscopy (Figures S32-S33) revealed that a minimum of 0.06 equivalents of ethylene were enclathrated. The large difference in occupancy estimates between SCXRD/TGA and <sup>1</sup>H NMR is likely due to the low solubility of ethylene in CDCl<sub>3</sub> and gas rapidly escaping the NMR solvent upon dissolution of the clathrate.



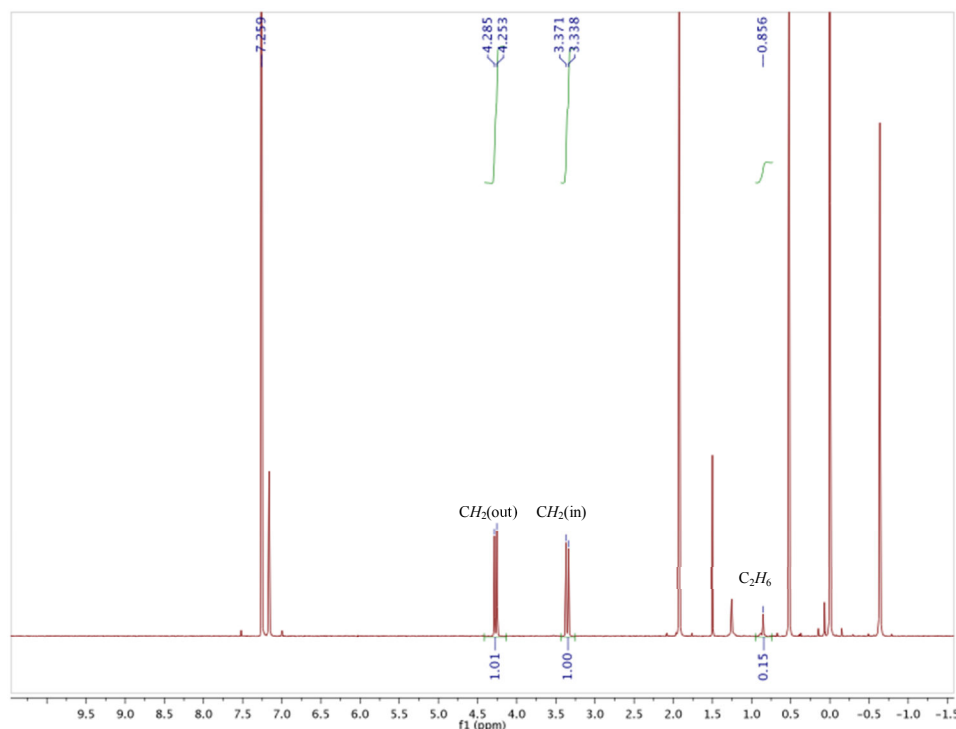
**Supporting Figure S32.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of  $x(\text{C}_2\text{H}_4)@\text{Me,H,SiMe}_2$  batch crystals at Day 0. The integrated area of the signal at 5.4 ppm equate to 0.06 equivalents of ethylene.



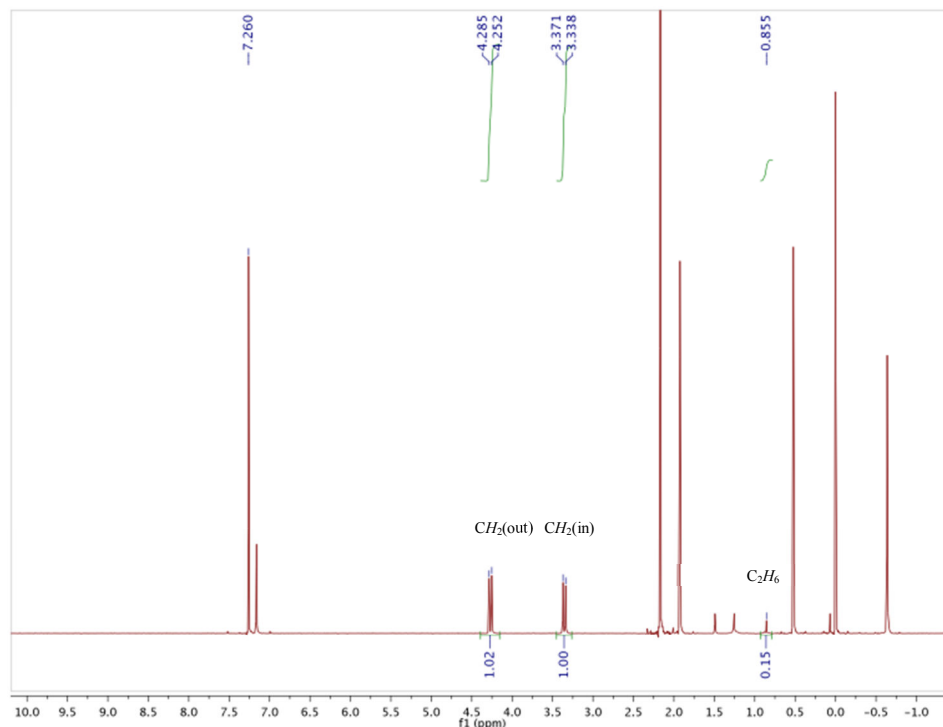
**Supporting Figure S33.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of  $x(\text{C}_2\text{H}_4)@\text{Me,H,SiMe}_2$  batch powder sample after seven days storage under ambient conditions. The integrated area of the signal at 5.4 ppm equate to 0.04 equivalents of ethylene.

**$x(\text{C}_2\text{H}_6)@\text{Me}_3\text{H}_2\text{SiMe}_2$**

Powdered  $x(\text{C}_2\text{H}_6)@\text{Me}_3\text{H}_2\text{SiMe}_2$  was prepared by the Bubbling to Dryness Method (above), by passing ethane gas through a solution of  $\text{Me}_3\text{H}_2\text{SiMe}_2$  until dryness. The powder was placed in a stream of nitrogen for 1 min. and was subsequently analyzed by  $^1\text{H}$  NMR spectroscopy (Figure S34) in  $\text{CDCl}_3$ , and again seven days later (Figure S35), revealing the enclathration of at least 0.056(5) equivalents of ethane and the retention of at least 0.055(4) equivalents of ethane after one week, respectively. Though they are reproducible, the  $^1\text{H}$  NMR spectra may underestimate the actual gas occupancy of the clathrate due to the low solubility of ethane in  $\text{CDCl}_3$  and gas rapidly escaping the NMR solvent upon dissolution of the clathrate.



**Supporting Figure S34.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a freshly prepared batch of  $x(\text{C}_2\text{H}_6)@\text{Me}_3\text{H}_2\text{SiMe}_2$  synthesized by the Bubbling to Dryness Method. The integrated area of the signal at 0.85 ppm equates to 0.06 equivalents of ethane.

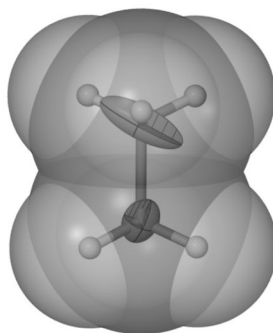


**Supporting Figure S35.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a preparation of  $x(\text{C}_2\text{H}_6)@\text{Me,H,SiMe}_2$  synthesized by the Bubbling to Dryness Method after seven days at ambient conditions. The integrated area of the signal at 0.85 ppm equates to 0.06 equivalents of ethane.

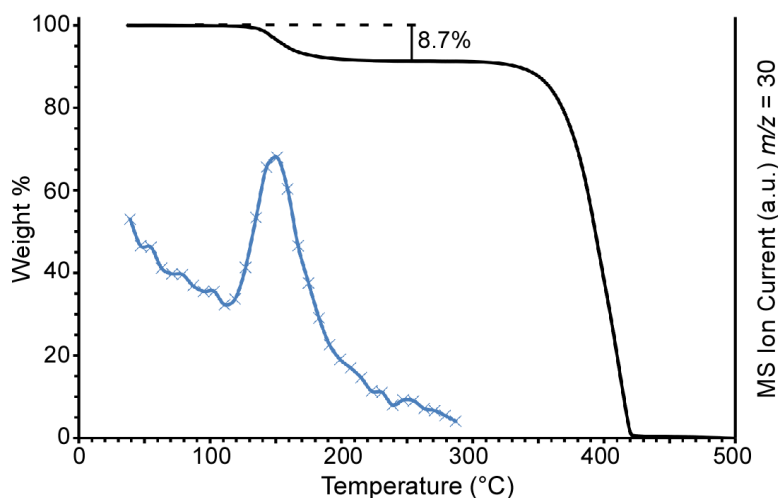
Single crystals of an ethane clathrate were prepared by the General Pressure Method (above) using 4.0 mL of  $\text{C}_2\text{H}_6$  ( $P_{\text{max(est.)}} \ll 40$  bar). This gave a single crystal of  $0.72(2)\text{C}_2\text{H}_6@\text{Me,H,SiMe}_2$  ( $0.60 \times 0.36 \times 0.35$  mm) that was analyzed by SCXRD immediately upon isolation. The thermal ellipsoid plot of the partial occupancy ethane molecule is given below; the freely refined C-C bond length measured  $1.500(6)$  Å. Due to librational effects, the unconstrained ethane C-C bond length is artificially short as compared to accepted values from electron diffraction and spectroscopy measurements, though it is similar to the value ( $1.510(2)$  Å) reported for SCXRD analysis of crystalline ethane at 85K.<sup>S10</sup> Open pan TGA studies on freshly prepared  $0.72(2)\text{C}_2\text{H}_6@\text{Me,H,SiMe}_2$  consistently showed weight loss % values that were as much as three times the expected mass loss (Figure S37) due to co-sublimation of the cavitant induced by ethane loss. Despite these inconsistencies, tandem TGA-MS analysis of the sample after 16 days at ambient conditions clearly shows the release of ethane ( $m/z = 30$  amu) to be the only detectable gas signal increase concomitant with the mass loss. Also, by placing a sample of the material in a sealed DSC pan (with punctured holes for gas escape) and using the same TGA protocol, a weight loss consistent with the SCXRD occupancy was observed (seen below for batch prepared by Defined Pressure Method - Figure S41).  $^1\text{H}$  NMR spectra of the dissolved batch crystals (Figure S38 and S39) at day 0 and 16 shows 0.38 and 0.35 equivalents of ethane, respectively. The differences in occupancies between SCXRD/TGA, and  $^1\text{H}$  NMR are likely due to the low solubility of ethane in  $\text{CDCl}_3$  and gas rapidly escaping the NMR solvent upon dissolution of the clathrate.

The original single crystal of  $0.72(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiH}_2$  ( $0.60 \times 0.36 \times 0.35$  mm), after storage under ambient conditions for 10 days, was re-analyzed by SCXRD, revealing an essentially identical structure (not reported). The ethane occupancy refined 0.73(3) and the C-C bond length measured 1.499(9) Å. Notably, the crystal showed no deterioration in diffraction quality after one week under ambient conditions as evidenced by the percent of observed reflection intensities (81% and 86% to  $2\theta = 56^\circ$  for the two collections, respectively).

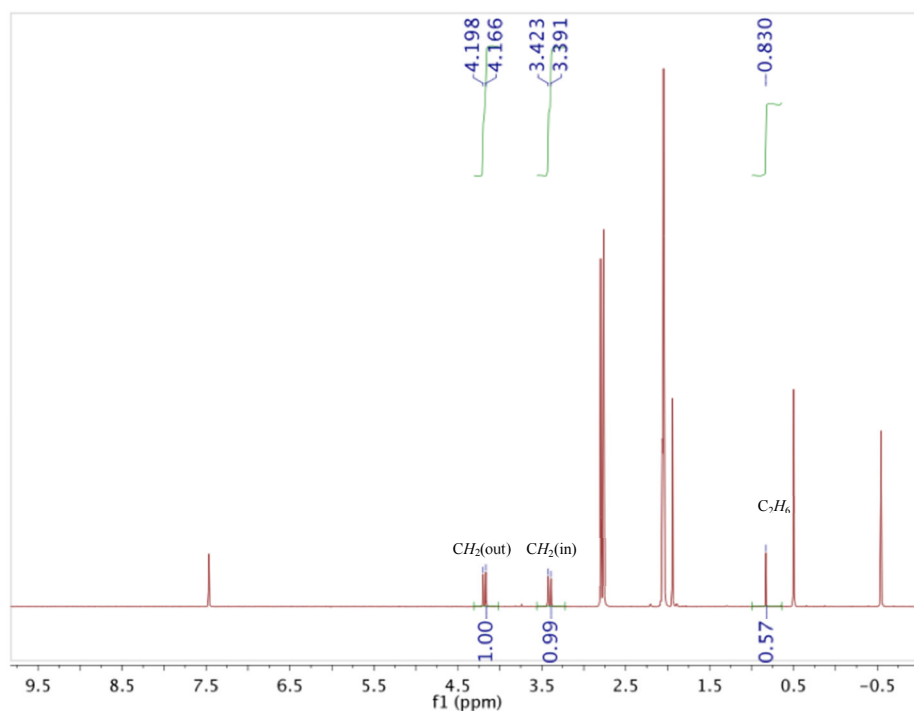
$0.72(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiH}_2$



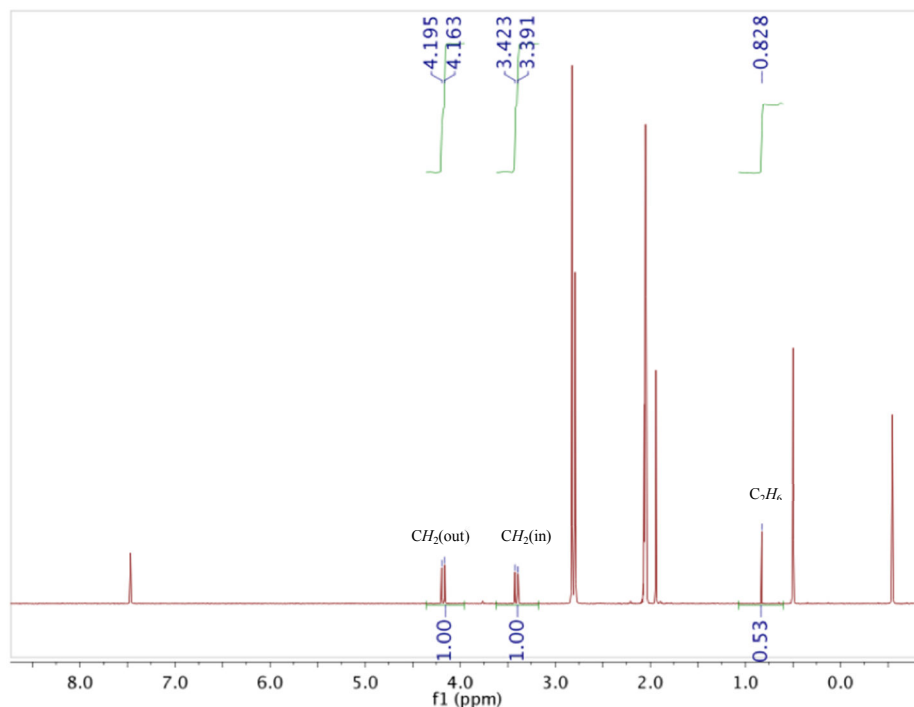
**Supporting Figure S36.** Thermal ellipsoid plots of the  $\text{C}_2\text{H}_6$  species in the single crystals of  $0.72(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiH}_2$ . Hydrogen atoms are placed in geometrically appropriate positions and were included in the refinement model.



**Supporting Figure S37.** TGA-MS [open pan] of  $0.72(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiH}_2$  after 16 days (black) and MS ion current at  $m/z = 30$  (blue). The continuous decrease in the background signal at  $m/z = 30$  is due to slow purging of residual  $^{15}\text{N}_2$  from residual nitrogen trapped in the furnace TGA furnace. An 8.7% mass loss equates to 2.3 equivalents of ethane, a value that is clearly artificially high due to induced co-sublimation of the host.



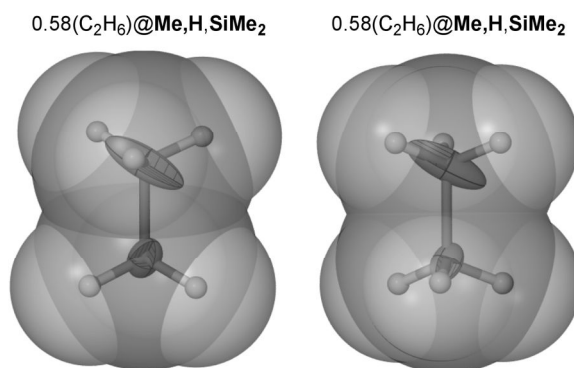
**Supporting Figure S38.** An exemplary  $^1\text{H}$  NMR spectrum (acetone- $\delta_6$ ) of a freshly prepared batch of  $0.72(\text{C}_2\text{H}_6)@\text{Me,H,SiMe}_2$  crystals synthesized by the Atmospheric Pressure Method at Day 0. The integrated area of the signal at 0.83 ppm equates to 0.38 equivalents of ethane.



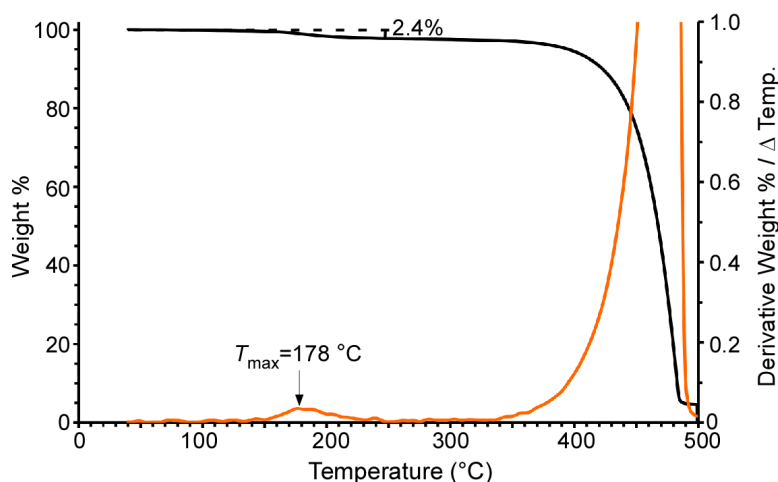
**Supporting Figure S39.** An exemplary  $^1\text{H}$  NMR spectrum (acetone- $\delta_6$ ) of a freshly prepared batch of  $0.72(\text{C}_2\text{H}_6)@\text{Me,H,SiMe}_2$  crystals synthesized by the Atmospheric Pressure Method at Day 16 under ambient conditions. The integrated area of the signal at 0.83 ppm equates to 0.35 equivalents of ethane.



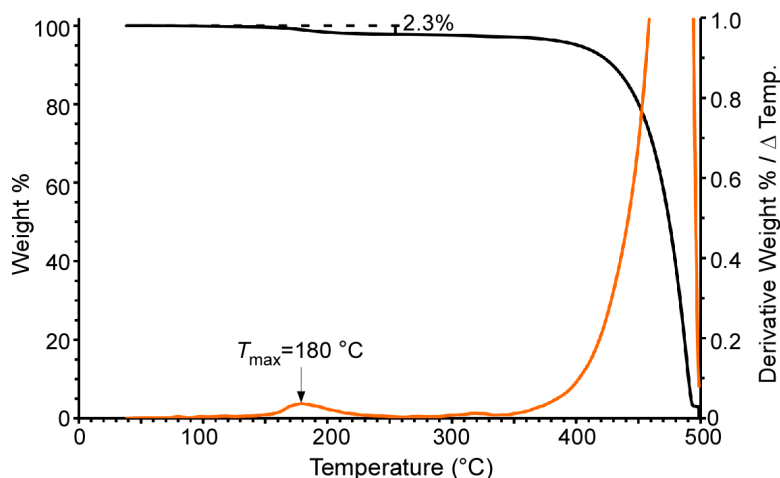
Single crystals of  $x(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiMe}_2$  were also prepared by the Defined Pressure Method (above) using a customized stainless steel bomb held at a fixed pressure of 9.8 bar. TGA analysis of the bulk sample, using punctured DSC pans, gave a reproducible mass loss of 2.4%, corresponding to loss of 0.63 equivalents of ethane (Figure S41). A single crystal of  $0.58(1)\text{C}_2\text{H}_6@\text{Me}_2\text{SiMe}_2$  ( $0.97\times0.56\times0.47$  mm) was isolated and its structure determined, giving a freely refined C-C bond length of  $1.491(8)$  Å. The crystal structure was then re-determined 11 days after isolation of the bulk sample, stored under ambient conditions, revealing the complete retention of ethane (refined  $0.58(1)$  eq.  $\text{C}_2\text{H}_6/\text{cavitand}$  and a C-C bond length of  $1.498(9)$  Å. The thermal ellipsoid plot of these collections are shown below (Figure S40). TGA analysis of the same sample, after storage of the sample for 11 days at room temperature, showed a 2.3% mass loss, corresponding to 0.60 equivalents of ethane (Figure S42).



**Supporting Figure S40.** Thermal ellipsoid plots of the  $\text{C}_2\text{H}_6$  species in the single crystals of (left to right) a)  $0.58(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiMe}_2$ , and b)  $0.58(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiMe}_2$  (re-determination of  $0.58(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiMe}_2$  after 11 days at ambient conditions). Hydrogen atoms are placed in geometrically appropriate positions and were included in the refinement model.



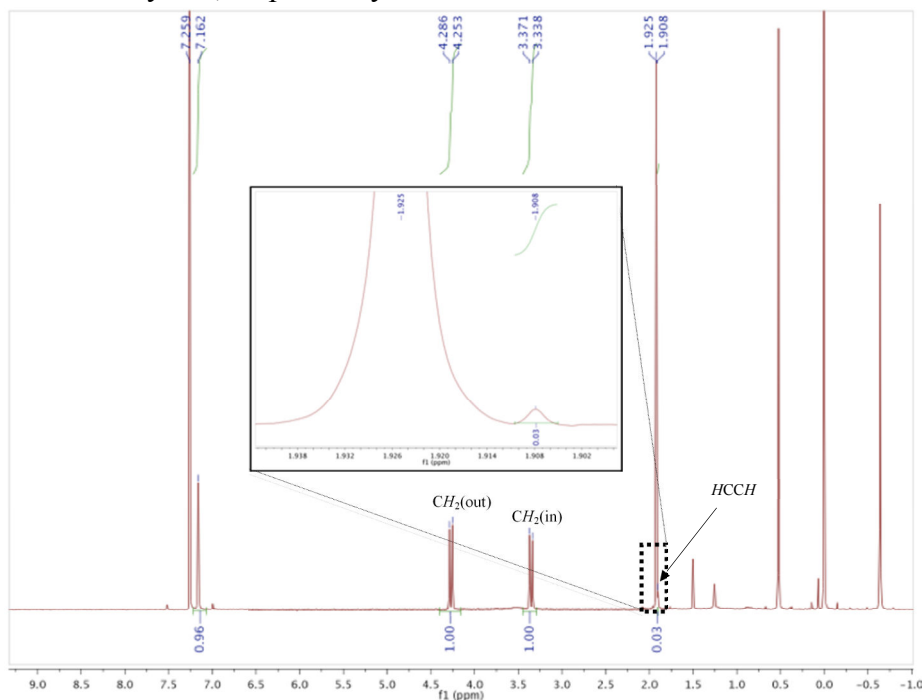
**Supporting Figure S41.** TGA [DSC pan technique] of  $0.58(\text{C}_2\text{H}_6)@\text{Me}_2\text{SiMe}_2$  (black) and derivative weight curve (orange) crystallized form saturated  $\text{CHCl}_3$  under 9.8 bar of  $\text{C}_2\text{H}_6$ . A 2.4% mass loss equates to 0.63 equivalents of ethane, a value in general agreement with SCXRD analysis.



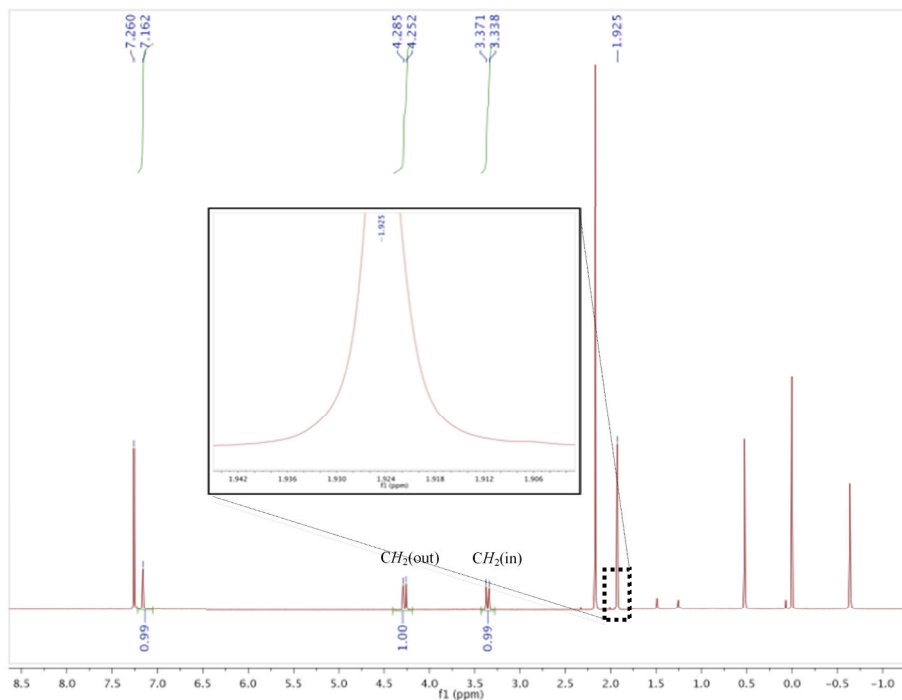
**Supporting Figure S42.** TGA [DSC pan technique] of  $0.58(\text{C}_2\text{H}_6)@\text{Me}_2\text{H}_2\text{SiMe}_2$  (black) and derivative weight curve (orange) crystallized form saturated  $\text{CHCl}_3$  under 9.8 bar of  $\text{C}_2\text{H}_6$  after 11 days. A 2.3% mass loss equates to 0.63 equivalents of ethane, a value in general agreement with SCXRD analysis.

### $x(\text{C}_2\text{H}_2)@\text{Me}_2\text{H}_2\text{SiMe}_2$

Acetylene gas, generated by the addition of water to calcium carbide, was passed through a saturated solution of  $\text{Me}_2\text{H}_2\text{SiMe}_2$  in  $\text{CHCl}_3$  (1 mL) until dryness (Bubbling to Dryness Method). The powder was placed in a stream of nitrogen for 1 minute and was subsequently analyzed by  $^1\text{H}$  NMR, and again seven days later (Figures S43 and S44, revealing the enclathration of at least 0.055(4) equivalents and zero equivalents of acetylene, respectively).



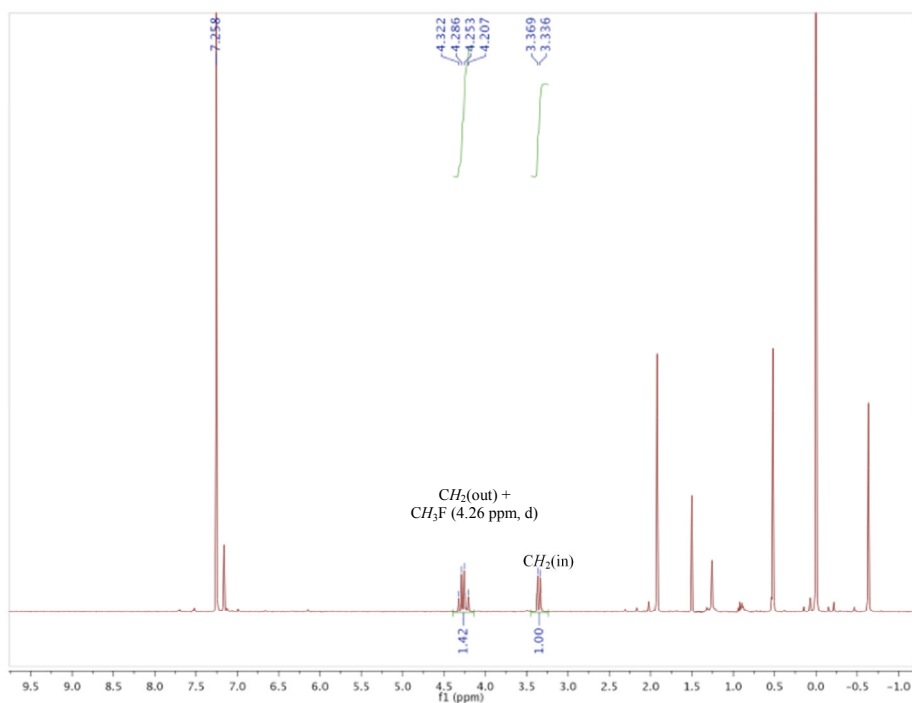
**Supporting Figure S43.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a “bubbling to dryness” preparation of  $x(\text{C}_2\text{H}_2)@\text{Me}_2\text{H}_2\text{SiMe}_2$ . The integrated area of the signal at 1.91 ppm equates to 0.06 equivalents of acetylene.



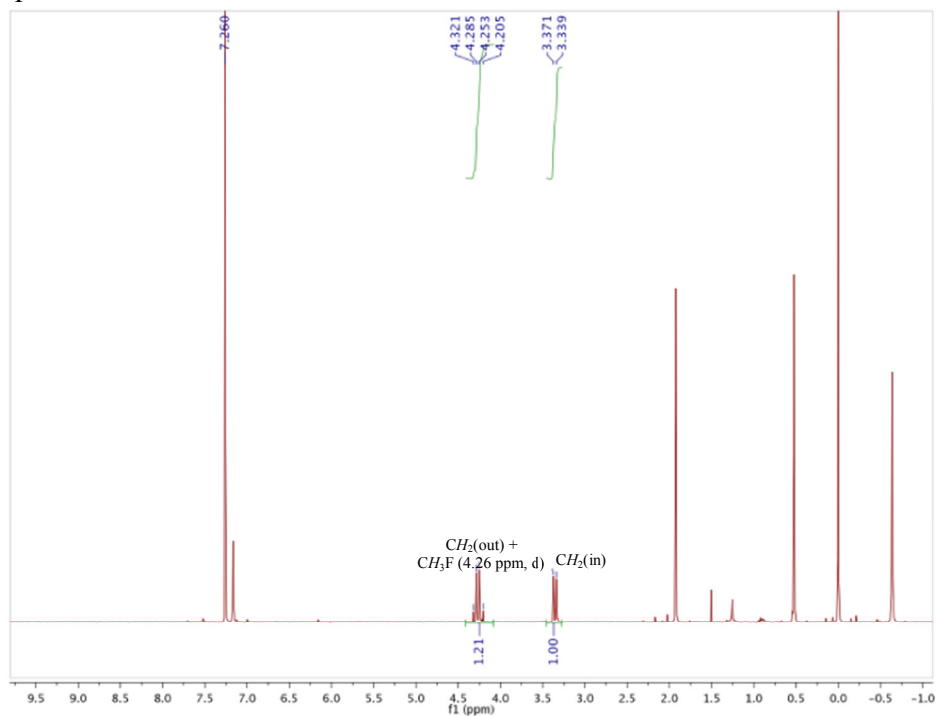
**Supporting Figure S44.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a “bubbling to dryness” preparation of  $x(\text{C}_2\text{H}_2)@\text{Me,H,SiMe}_2$  that was subsequently left at ambient conditions for seven days. The spectrum shows almost no trace of acetylene.

#### $x(\text{CH}_3\text{F})@\text{Me,H,SiMe}_2$

Powdered  $x(\text{CH}_3\text{F})@\text{Me,H,SiMe}_2$  was prepared by the Bubbling to Dryness Method (above), by passing fluoromethane gas through a solution of  $\text{Me,H,SiMe}_2$  until dryness. The powder was placed in a stream of nitrogen for 1 min. and was subsequently analyzed by  $^1\text{H}$  NMR spectroscopy (Figure S45) in  $\text{CDCl}_3$ , and again seven days later (Figure S46), revealing the enclathration of 0.56 equivalents of fluoromethane and the retention of at least 0.28 equivalents of fluoromethane after one week, respectively.

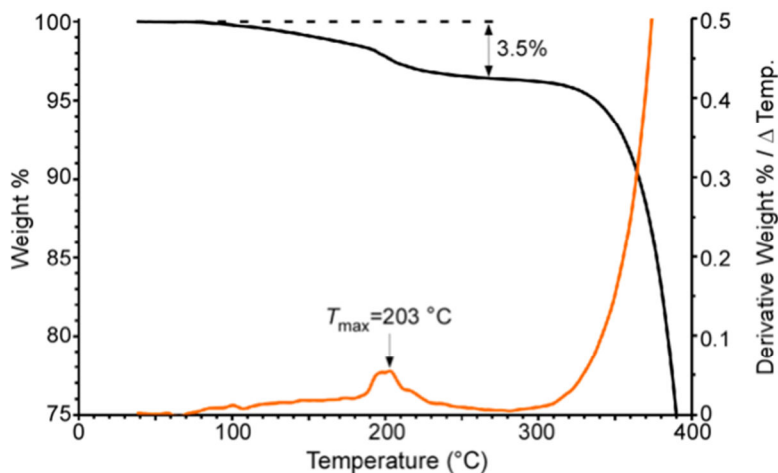


**Supporting Figure S45.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a Day 0 “bubbling to dryness” preparation of  $x(\text{CH}_3\text{F})@\text{Me}_2\text{H}_2\text{SiMe}_2$  (1 atm  $\text{CH}_3\text{F}$ ). The integrated area of the signal at 4.26 ppm subtracted from the signal at 3.4 ppm equates to 0.56 equivalents of fluoromethane.



**Supporting Figure S46.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a Day 7 “bubbling to dryness” preparation of  $x(\text{CH}_3\text{F})@\text{Me}_2\text{H}_2\text{SiMe}_2$  (1 atm  $\text{CH}_3\text{F}$ ). The integrated area of the signal at 4.26 ppm subtracted from the signal at 3.4 ppm equates to 0.28 equivalents of fluoromethane.

Single crystals the partial fluoromethane clathrate of **Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>** were obtained by the Atmospheric Pressure Method which involved bubbling fluoromethane gas into a near-saturated solution (0.10 M) of **Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>** in CHCl<sub>3</sub> until a precipitate formed, capping the glass vial and reheating to dissolve the remaining precipitate, after which crystals formed over a period of hours to days. X-ray structure determination on one single crystal (1.49×0.38×0.26 mm) gave an estimated fluoromethane occupancy of 0.80(4)CH<sub>3</sub>F@**Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>** (Table S4). Analysis of other crystals from different batches prepared in the same manner gave the same occupancies of fluoromethane, within the estimated error. TGA analysis of the bulk material upon isolation showed a mass loss of 3.5%, attributed to 0.82 eq. of fluoromethane (Figure S47). Data collection on another crystal (0.86×0.67×0.29 mm) from the original batch, but after keeping the crystals in an open container at ambient conditions for 146 days, gave an estimated fluoromethane occupancy of 0.37 eq. There is an indication from the data—apparent elongation of the C-F bond, greater than expected electron density at the carbon position relative to the fluorine position—that the crystals had also seemingly taken up a small amount ~0.14 eq. of atmospheric water vapor during this time. In analogy to the emptying of the partial hydrate crystals, the 0.37(CH<sub>3</sub>F),0.14(H<sub>2</sub>O)@**Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>** crystal was heated at 150°C (228°C above the boiling point of CH<sub>3</sub>F) for four days and its structure was re-determined at 100 K by SCXRD; the occupancy was found to be 0.23 eq. CH<sub>3</sub>F per cavitant, with no evidence of residual water. Subsequent heating of the same crystal at 190°C for 1 more week yielded the empty **Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>** crystal as shown by SCXRD analysis. Being redundant with the reported empty **Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>** structure, the latter collection has been omitted from the crystallographic data tables. Notably, the crystal showed almost no deterioration in diffraction quality upon CH<sub>3</sub>F/H<sub>2</sub>O loss induced by heating, as evidenced by the percent of observed reflection intensities (70% and 68% to 2θ = 56° for 0.37(CH<sub>3</sub>F),0.14(H<sub>2</sub>O)@**Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>**, and 0.24(1)CH<sub>3</sub>F@**Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>**, respectively).

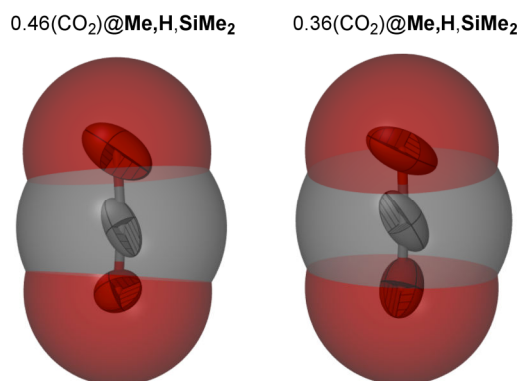


**Supporting Figure S47.** TGA [open pan] of 0.80(CH<sub>3</sub>F)@**Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>** at Day 0 (black) and derivative weight curve (orange). The 3.5% mass loss equates to 0.82 equivalents of CH<sub>3</sub>F.

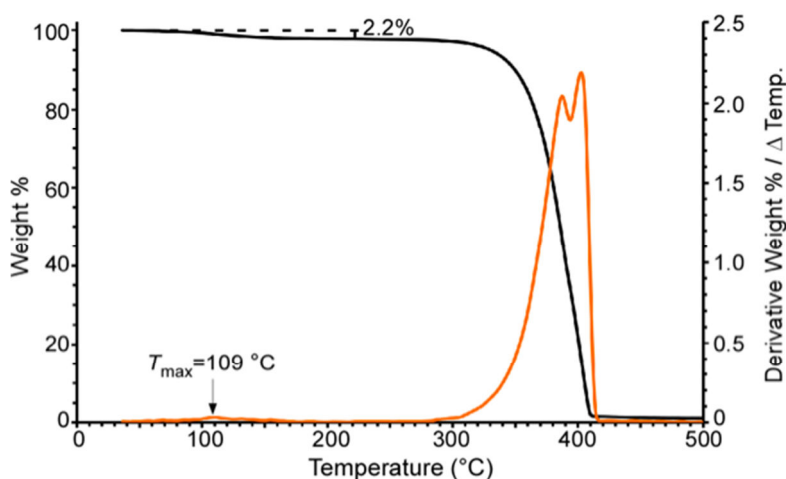
#### ***xCO<sub>2</sub>@Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>***

Single crystals of a partial carbon dioxide clathrate were prepared by the General Pressure Method. Approximately 5 g of CO<sub>2</sub> (P<sub>max(est.)</sub> ≤ 61 bar) was enclosed with a 1 mL saturated solution of **Me<sub>6</sub>H<sub>2</sub>SiMe<sub>2</sub>** in CHCl<sub>3</sub>, with activated 3 Å molecular sieves in an uncapped glass vial (1.5 mL capacity), in a Teflon digestion bomb. Allowing the system to equilibrate to room temperature over a period of several days afforded crystals of the partial carbon dioxide clathrate. One single crystal

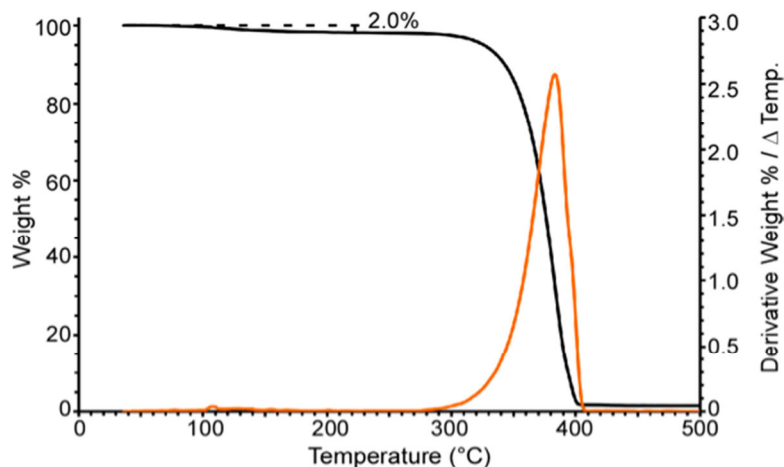
(0.64×0.51×0.20 mm) was analyzed by SCXRD immediately upon isolation and gave a refined composition (atom occupancy refinement and SQUEEZE analysis) of 0.46(6)CO<sub>2</sub>@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>. The same crystal, analyzed by SCXRD after 10 days exposure to ambient conditions was estimated to contain 0.36(6) equivalents of CO<sub>2</sub>. The thermal ellipsoid plots are shown below (Figure S48). TGA studies on the bulk powder sample treated in the same way show mass losses of slightly lower occupancy (0.28 eq. and 0.25 eq. after 7 days) (Figures S49-S50) with the SCXRD data (0.47 equivalents, by mass, upon isolation and 0.36 equivalents, by mass, after 7 days). Tandem TGA-MS measurements were made on a 2<sup>nd</sup> batch of x(CO<sub>2</sub>)@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> that clearly shows the release of CO<sub>2</sub> (*m/z* = 44 amu) to be concomitant with the mass loss (Figure S51).



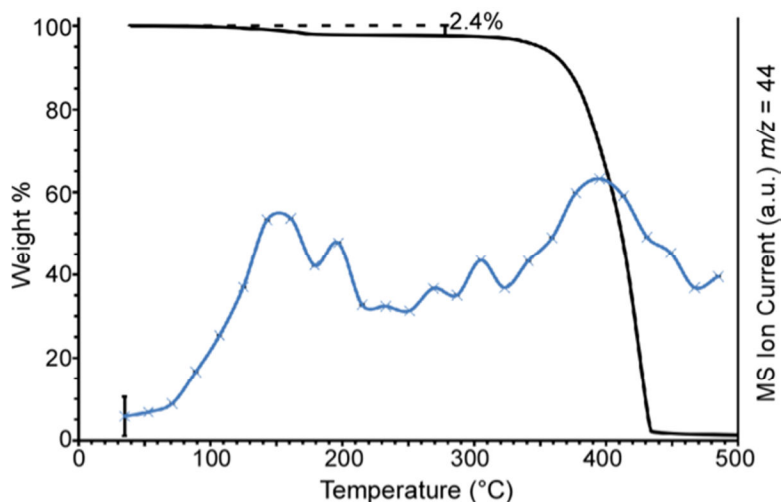
**Supporting Figure S48.** Thermal ellipsoid plot of the CO<sub>2</sub> species in the single crystals of 0.46(CO<sub>2</sub>)@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> and 0.36(CO<sub>2</sub>)@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>, redetermined after 10 days at ambient conditions. The CO<sub>2</sub> molecule was constrained to be linear in the refinement of the 0.36(CO<sub>2</sub>)@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> data.



**Supporting Figure S49.** TGA [open pan] of 0.47(CO<sub>2</sub>)@Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub> at Day 0 (black) and derivative weight curve (orange). A 2.2% mass loss equates to 0.28 equivalents of CO<sub>2</sub>.



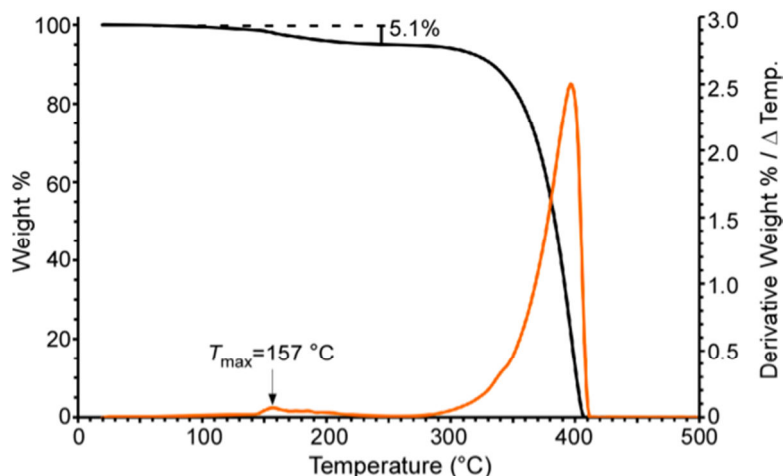
**Supporting Figure S50.** TGA [open pan] of  $0.36(\text{CO}_2)@ \text{Me,H,SiMe}_2$  after 7 days (black) and derivative weight curve (orange). The 2.0% mass loss equates to 0.25 equivalents of  $\text{CO}_2$ .



**Supporting Figure S51.** TGA [open pan] of a sample from a 2<sup>nd</sup> batch preparation of  $x(\text{CO}_2)@ \text{Me,H,SiMe}_2$  at Day 0 (black) and MS ion current at  $m/z = 44$  (blue). The error bars in the first mass spectrometry data point indicate two standard deviations of the signal current for the 30 minutes prior to heating. A 2.4% mass loss equates to 0.30 equivalents of  $\text{CO}_2$ .

### $x(\text{H}_2\text{S})@ \text{Me,H,SiMe}_2$

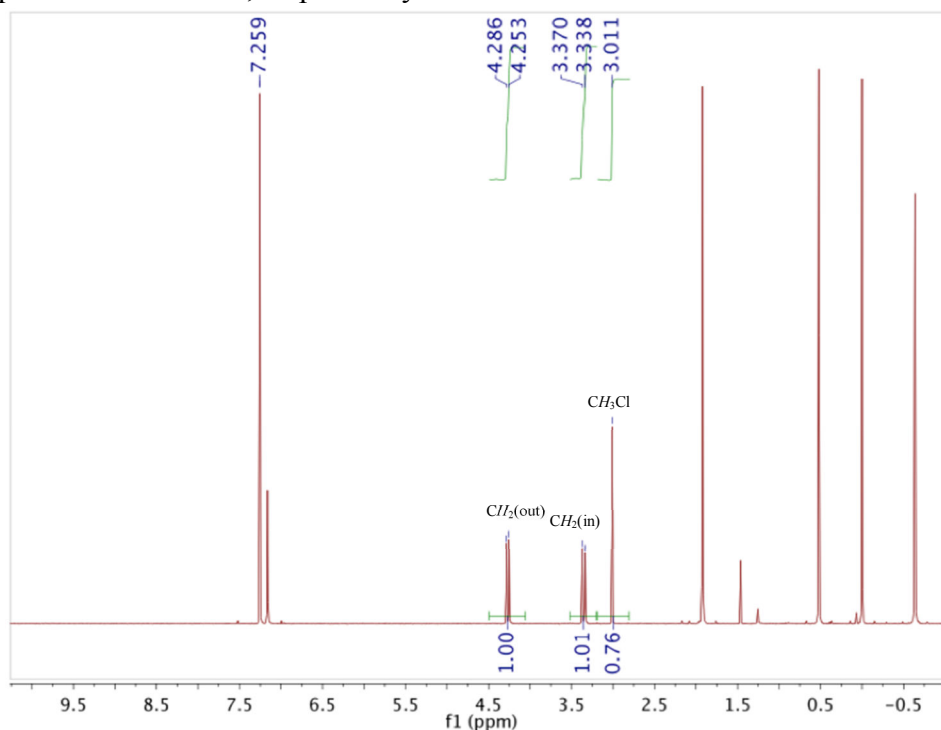
Hydrogen sulfide clathrate crystals were grown under the Atmospheric Pressure Method, under 1 atm of gas, as outlined above. Single crystals that formed over a period of days were analyzed by SCXRD giving a refined composition of  $0.82(\text{H}_2\text{S})@ \text{Me,H,SiMe}_2$  (Table S4). The thermal ellipsoid plot is provided below. TGA studies (open pan) show a mass loss corresponding to 1.21 eq.  $\text{H}_2\text{S}$  (grown from chloroform solution) (Figure S52), due to co-sublimation of the host concomitant with  $\text{H}_2\text{S}$  loss.



**Supporting Figure S52.** TGA [open pan] of 0.82(H<sub>2</sub>S)@Me,H,SiMe<sub>2</sub> (black) and derivative weight curve (orange). The 5.1% mass loss equates to 1.21 equivalents of H<sub>2</sub>S.

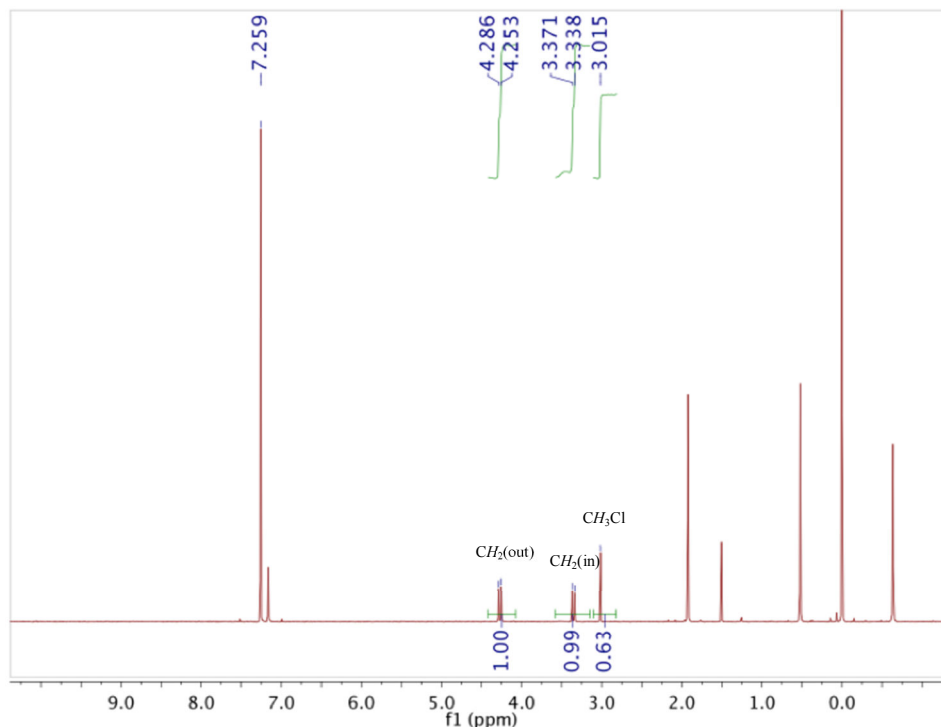
### **CH<sub>3</sub>Cl@Me,H,SiMe<sub>2</sub>**

Chloromethane was bubbled into a saturated solution of Me,H,SiMe<sub>2</sub> in CHCl<sub>3</sub> (1 mL) until dryness (Bubbling to Dryness Method). The powder was placed in a stream of nitrogen for 1 min. and analyzed by <sup>1</sup>H NMR after nitrogen purge (Figure S53) and 7 days later (Figure S54). These show occupancies of 1.0 and 0.84 eq. of chloromethane, respectively.



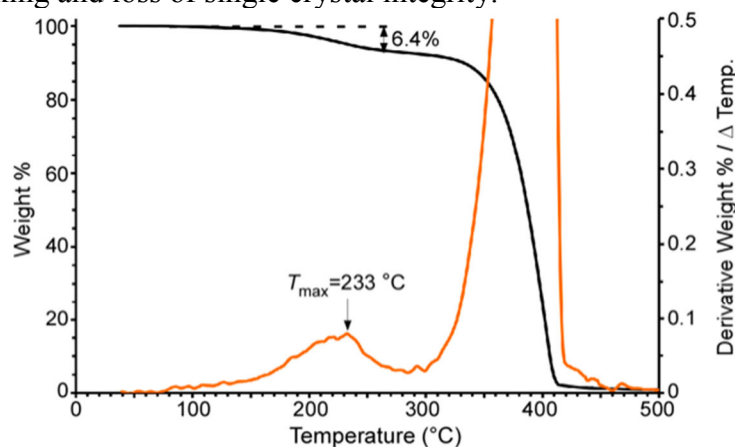
**Supporting Figure S53.** An exemplary <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, w. TMS) of a Day 0 “bubbling to dryness” preparation of x(CH<sub>3</sub>Cl)@Me,H,SiMe<sub>2</sub> (1 atm CH<sub>3</sub>Cl). The integrated area of the signal at 3.05 ppm equates to 1.01 equivalents of chloromethane.





**Supporting Figure S54.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a Day 7 “bubbling to dryness” preparation of  $x(\text{CH}_3\text{Cl})@\text{Me,H,SiMe}_2$  (1 atm  $\text{CH}_3\text{Cl}$ ). The integrated area of the signal at 3.05 ppm equates to 0.84 equivalents of chloromethane.

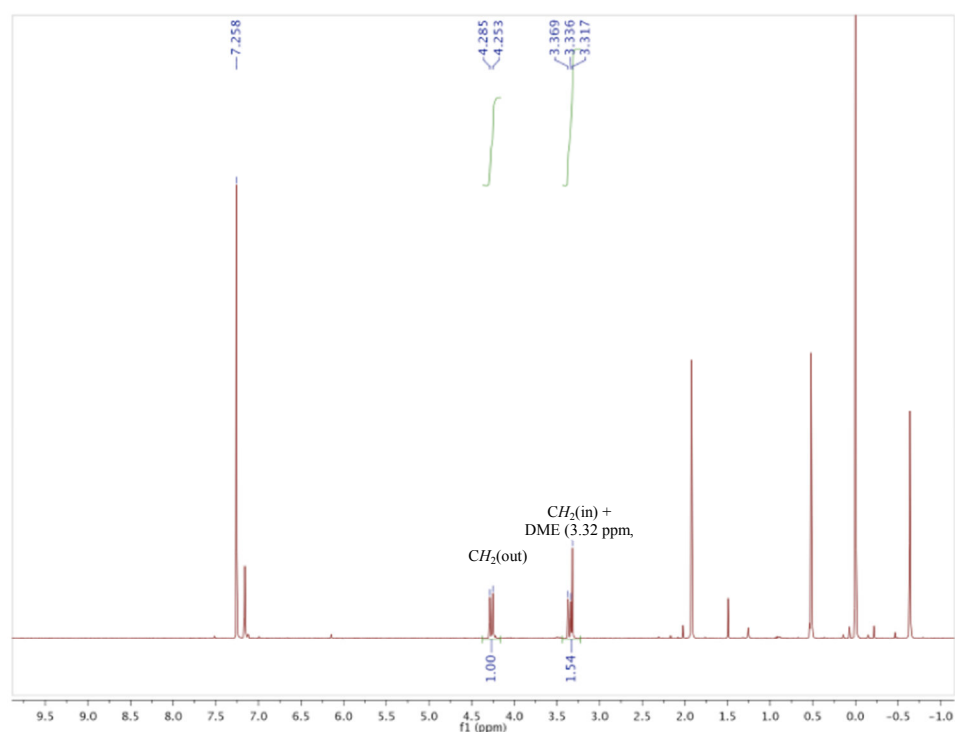
A batch sample of the chloromethane clathrate was prepared by the Atmospheric Pressure Method outlined above. Single crystals that formed over a period of days were analyzed by SCXRD and gave a refined composition of  $\text{CH}_3\text{Cl}@\text{Me,H,SiMe}_2$  (Table S4). Single crystals of the chloromethane clathrate were also grown from ethyl acetate using the same method and were shown to be also be fully occupied by chloromethane (Table S4). For a thermal ellipsoid plot, see Figure 2 in the paper. TGA studies show a mass loss corresponding to 1.0 eq.  $\text{CH}_3\text{Cl}$  (grown from chloroform solution) (Figure S55). An attempt to degas  $\text{CH}_3\text{Cl}@\text{Me,H,SiMe}_2$  in a single-crystal-to-single-crystal by heating the crystal at  $150^\circ\text{C}$  resulted in crystal cracking and loss of single crystal integrity.



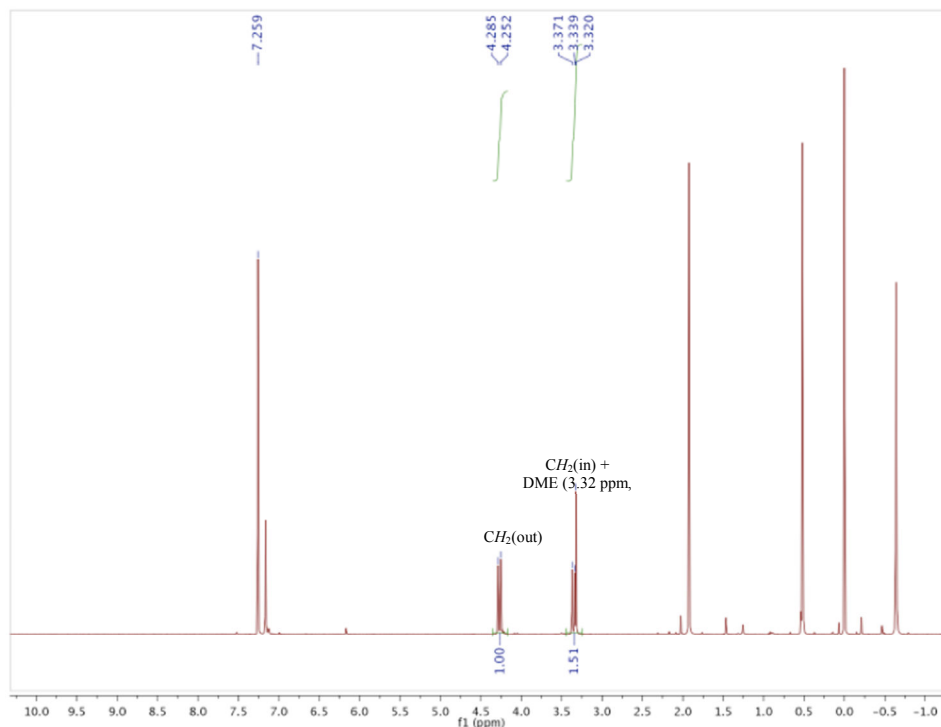
**Supporting Figure S55.** TGA [open pan] of  $\text{CH}_3\text{Cl}@\text{Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). The 6.4% mass loss equates to 1.0 equivalents of  $\text{CH}_3\text{Cl}$ .

***0.82(CH<sub>3</sub>OCH<sub>3</sub>)@Me,H,SiMe<sub>2</sub>***

Dimethylether (DME) was bubbled into a saturated solution of **Me,H,SiMe<sub>2</sub>** in CHCl<sub>3</sub> (1 mL) until dryness (Bubbling to Dryness Method). The powder was placed in a stream of nitrogen for 1 min. and then analyzed by <sup>1</sup>H NMR after nitrogen purge (Figure S56) (0.36 eq.) and after 7 days (Figure S57) (0.34 eq.).

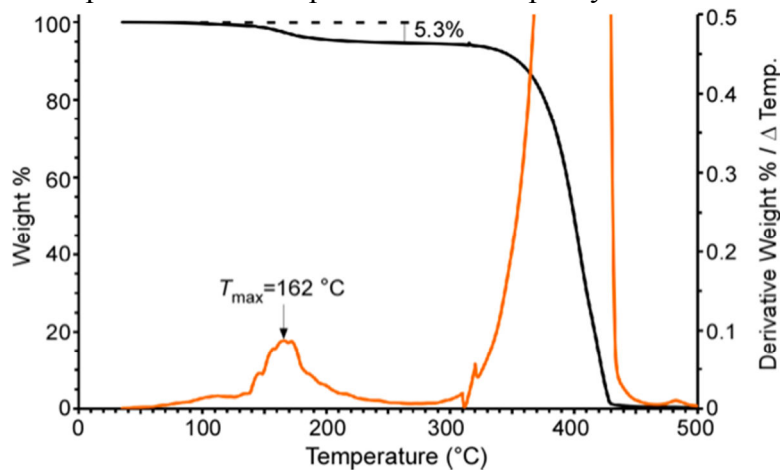


**Supporting Figure S56.** An exemplary <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, w. TMS) of a Day 0 “bubbling to dryness” preparation of *x*(C<sub>2</sub>H<sub>6</sub>O)@**Me,H,SiMe<sub>2</sub>** (1 atm C<sub>2</sub>H<sub>6</sub>O). The integrated area of the signal at 3.32 ppm subtracted from the signal at 4.3 ppm equates to 0.36 equivalents of dimethylether.



**Supporting Figure S57.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a Day 7 “bubbling to dryness” preparation of  $x(\text{C}_2\text{H}_6\text{O})@\text{Me,H,SiMe}_2$  (1 atm  $\text{C}_2\text{H}_6\text{O}$ ). The integrated area of the signal at 3.32 ppm subtracted from the signal at 4.3 ppm equates to 0.34 equivalents of dimethylether.

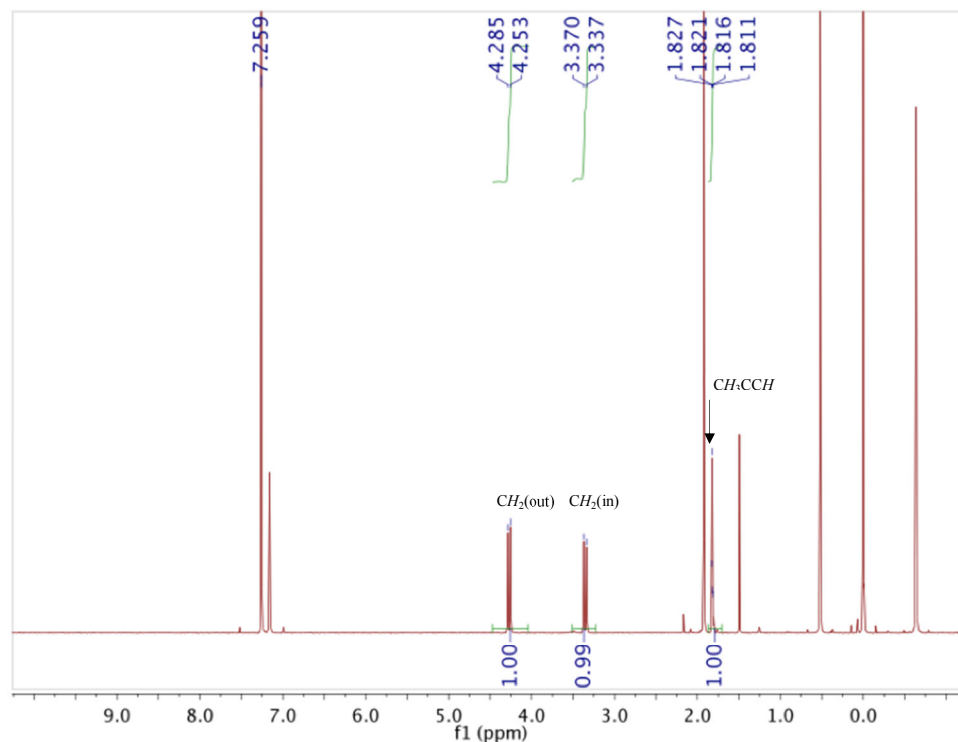
Attempts to grow single crystals of a dimethylether clathrate by the Atmospheric Pressure Method were generally unsuccessful, yielding single crystal of the partial cavitand hydrate. Single crystals of a DME clathrate were prepared by the elevated pressure method defined above using 3 mL of  $\text{CH}_3\text{OCH}_3$  ( $P_{\text{max(est.)}} \leq 6$  bar). This gave single crystals of  $0.82(\text{CH}_3\text{OCH}_3)@\text{Me,H,SiMe}_2$  that were analyzed by SCXRD upon isolation (Table S4). TGA studies show a mass loss of 0.93 eq. dimethylether (Figure S58), slightly higher than expected when compared to the occupancy determined by SCXRD.



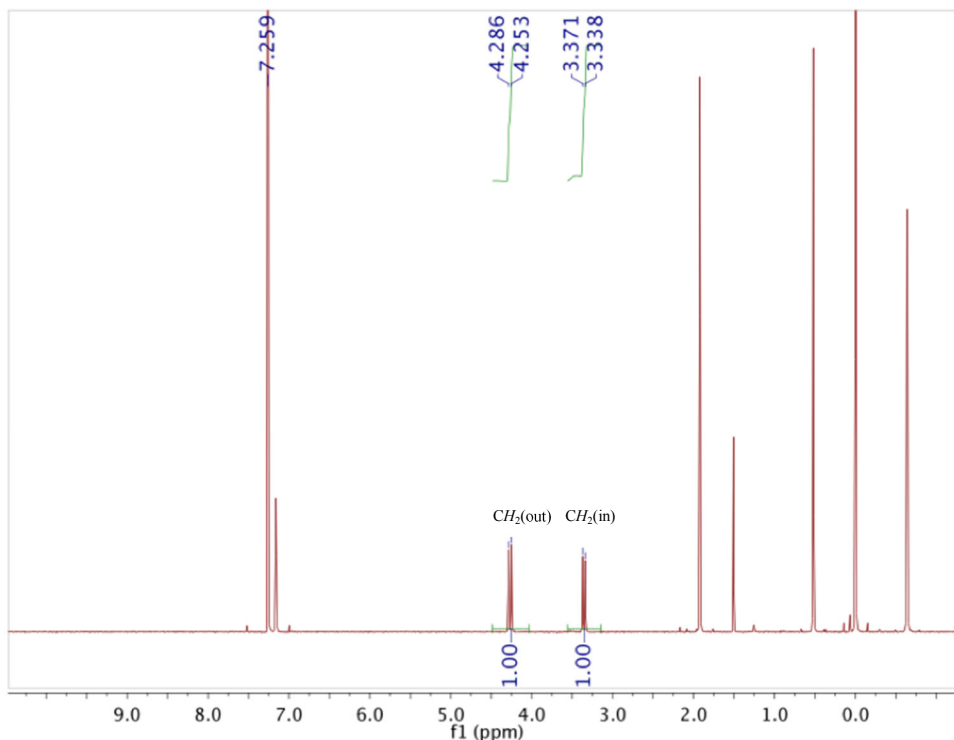
**Supporting Figure S58.** TGA [open pan] of  $0.82(\text{CH}_3\text{OCH}_3)@\text{Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). The 5.3% mass loss equates to 0.93 equivalents of DME.

***CH<sub>3</sub>CCH@Me,H,SiMe<sub>2</sub>•2CHCl<sub>3</sub>***

Propyne was bubbled into a saturated solution of **Me,H,SiMe<sub>2</sub>** in CHCl<sub>3</sub> (1 mL) until dryness (Bubbling to Dryness Method). The powder was placed in a stream of nitrogen for 1 min., analyzed by <sup>1</sup>H NMR (Figure S59) and again after 7 days (Figure S60). <sup>1</sup>H NMR analysis at day 0 shows 1 eq. of propyne per cavitand and no propyne remains at day 7.

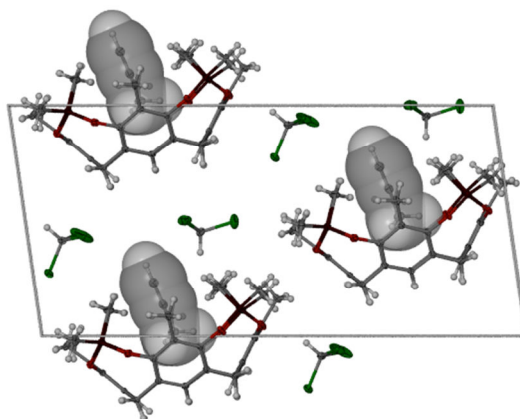


**Supporting Figure S59.** An exemplary <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, w. TMS) of a Day 0 “bubbling to dryness” preparation of *x*(CH<sub>3</sub>CCH)@**Me,H,SiMe<sub>2</sub>** (1 atm CH<sub>3</sub>CCH). The integrated area of the signal at 1.8 ppm equates to 1.00 equivalent of propyne.

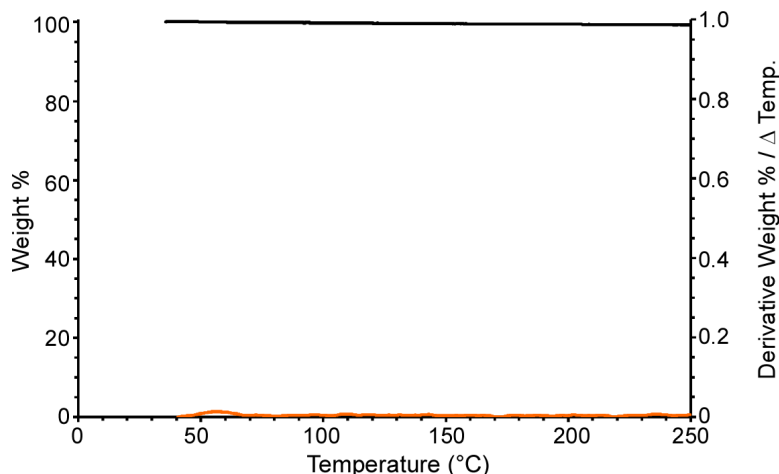


**Supporting Figure S60.** An exemplary  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of a Day 7 “bubbling to dryness” preparation of  $x(\text{CH}_3\text{CCH})@\text{Me,H,SiMe}_2$  (1 atm  $\text{CH}_3\text{CCH}$ ). The absence of a peak at 1.8 ppm suggests that all propyne bound at day 0, has been lost over a week’s time.

Single crystals of the propyne clathrate were grown under the ambient conditions method outlined above. SCXRD analysis of the crystals gave a composition of  $\text{CH}_3\text{CCH}@\text{Me,H,SiMe}_2 \cdot 2\text{CHCl}_3$  (Table S4). Upon visual inspection, the crystals rapidly decomposed under ambient conditions. TGA of the sample showed almost no mass (0.5%) loss up to  $250^\circ\text{C}$  (Figure S62). This illustrates that there is no remaining propyne/chloroform in the solid material.



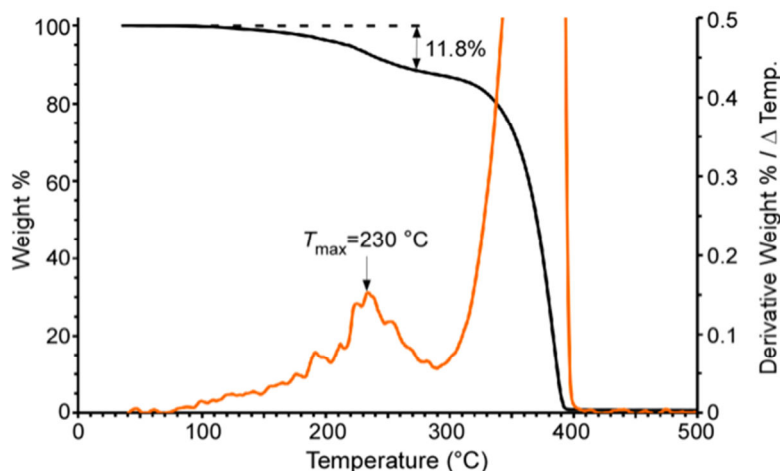
**Supporting Figure S61.** Crystal structure of propyne and chloroform molecules in a  $P2_1/n$  space group setting collected at 100 K. Atoms are shown as thermal ellipsoids shown at 50% probability level for thermal ellipsoids (gray – carbon, red – oxygen, maroon – silicon, white – hydrogen, green - chlorine).



**Supporting Figure S62.** TGA [open pan] of  $\text{CH}_3\text{CCH@Me,H,SiMe}_2 \cdot 2\text{CHCl}_3$  at Day 0 (black) and derivative weight curve (orange). The lack of mass loss is attributed to the instability of the clathrate under ambient conditions and is therefore near 0.0% since the chloroform and propyne guests have essentially escaped upon preparing the sample for TGA analysis.

#### **$\text{CH}_3\text{Br@Me,H,SiMe}_2$**

Crystals of a bromomethane clathrate were grown by the Atmospheric Pressure Method outlined above. Single crystals that formed over a period of days were analyzed by SCXRD and gave a refined composition of  $\text{CH}_3\text{Br@Me,H,SiMe}_2$  (Table S4). For a thermal ellipsoid plot, see Figure 2 in the paper. TGA studies show a mass loss of approximately 1 eq.  $\text{CH}_3\text{Br}$  per cavitand (Figure S63).



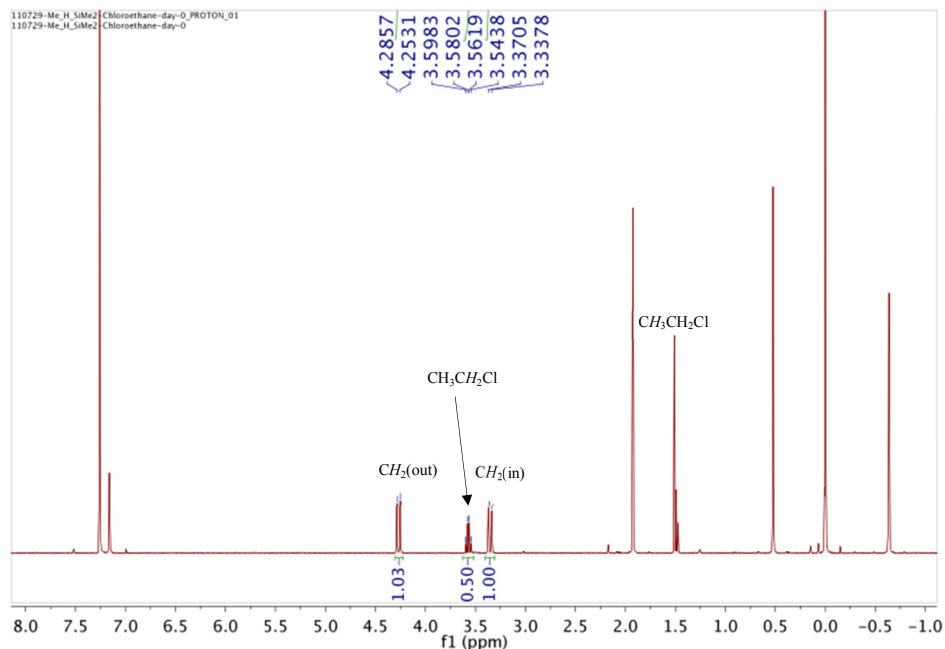
**Supporting Figure S63.** TGA [open pan] of  $\text{CH}_3\text{Br@Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). The 11.8% mass loss equates to 1.1 equivalents of  $\text{CH}_3\text{Br}$ .

#### **$0.83(\text{CH}_3\text{SH})\text{@Me,H,SiMe}_2$**

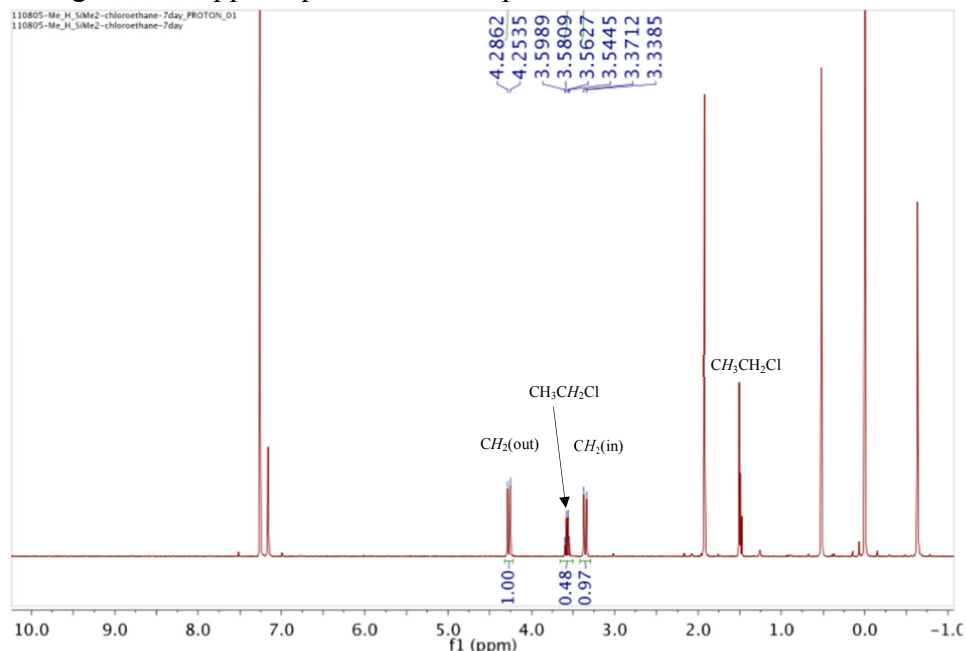
Crystals of a methanethiol clathrate were grown by the Atmospheric Pressure Method outlined above. Single crystals that formed over a period of days were analyzed by SCXRD and gave a refined composition of  $0.83(\text{CH}_3\text{SH})\text{@Me,H,SiMe}_2$  (Table S4). TGA of the material gave mass losses far greater than what was expected by the occupancy determined by SCXRD.

### *EtCl@Me,H,SiMe<sub>2</sub>*

Chloroethane was bubbled into a saturated solution of **Me,H,SiMe<sub>2</sub>** in CHCl<sub>3</sub> (1 mL) until dryness (Bubbling to Dryness Method). The powder was placed in a stream of nitrogen for 1 min. and then analyzed by <sup>1</sup>H NMR after nitrogen purge (Figure S64) (1.0 eq.) and after 7 days (Figure S65) (0.34 eq.).

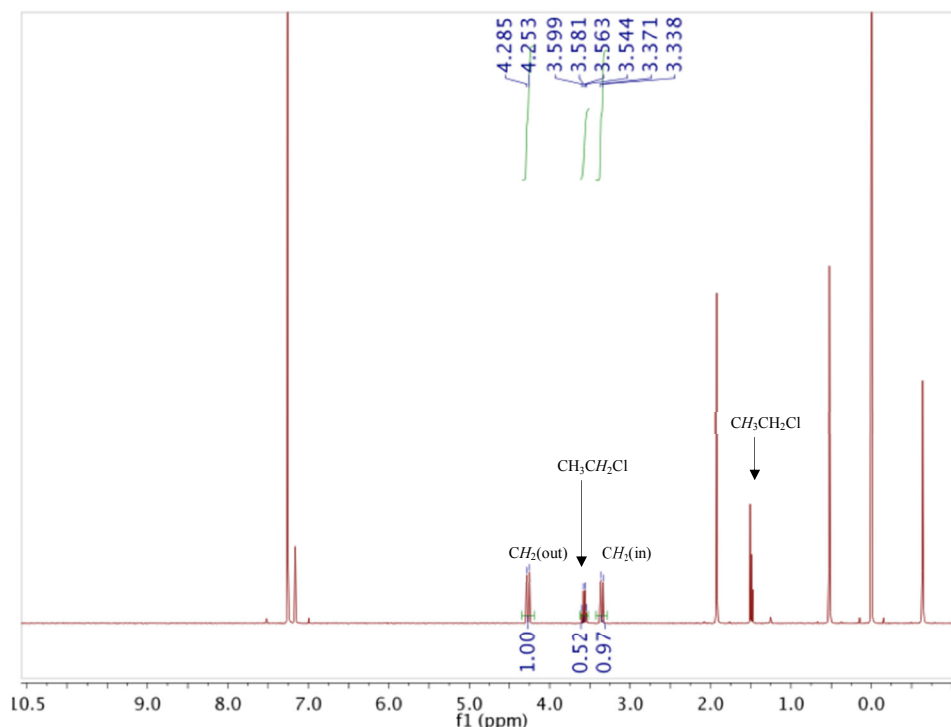


**Supporting Figure S64.** An exemplary <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, w. TMS) of a Day 0 “bubbling to dryness” preparation of *x*(EtCl)@**Me,H,SiMe<sub>2</sub>** (1 atm EtCl). The integrated area of the signal at 1.8 ppm equates to 1.00 equivalent of chloroethane.

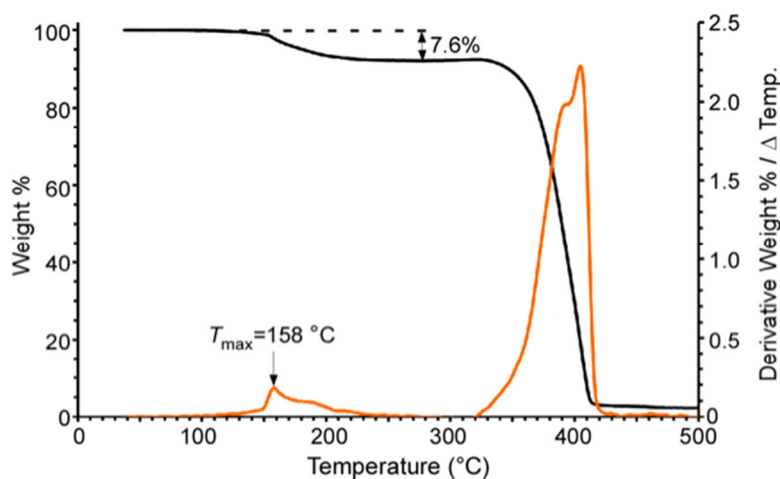


**Supporting Figure S65.** An exemplary <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, w. TMS) of a Day 7 “bubbling to dryness” preparation of *x*(EtCl)@**Me,H,SiMe<sub>2</sub>** (1 atm EtCl). The integrated area of the signal at 1.8 ppm equates to approximately 0.96 equivalent of chloroethane.

A saturated solution of **Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** in CHCl<sub>3</sub> (1 mL) was placed in a glass screw cap vial with 5 mL of EtCl (liq.) and sealed ( $P \approx 2$  atm). Single crystals began to form within 1 hour and were harvested after two days. SCXRD analysis gave a composition of EtCl@**Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** (Table S4). A thermal ellipsoid plot can be seen in Figure 2. <sup>1</sup>H NMR analysis of the crystals shows 1.04 eq. of EtCl per cup (Figure S66). TGA analysis of the crystals shows 7.6% mass loss corresponding to 0.98 eq. of EtCl per cup (Figure S67).

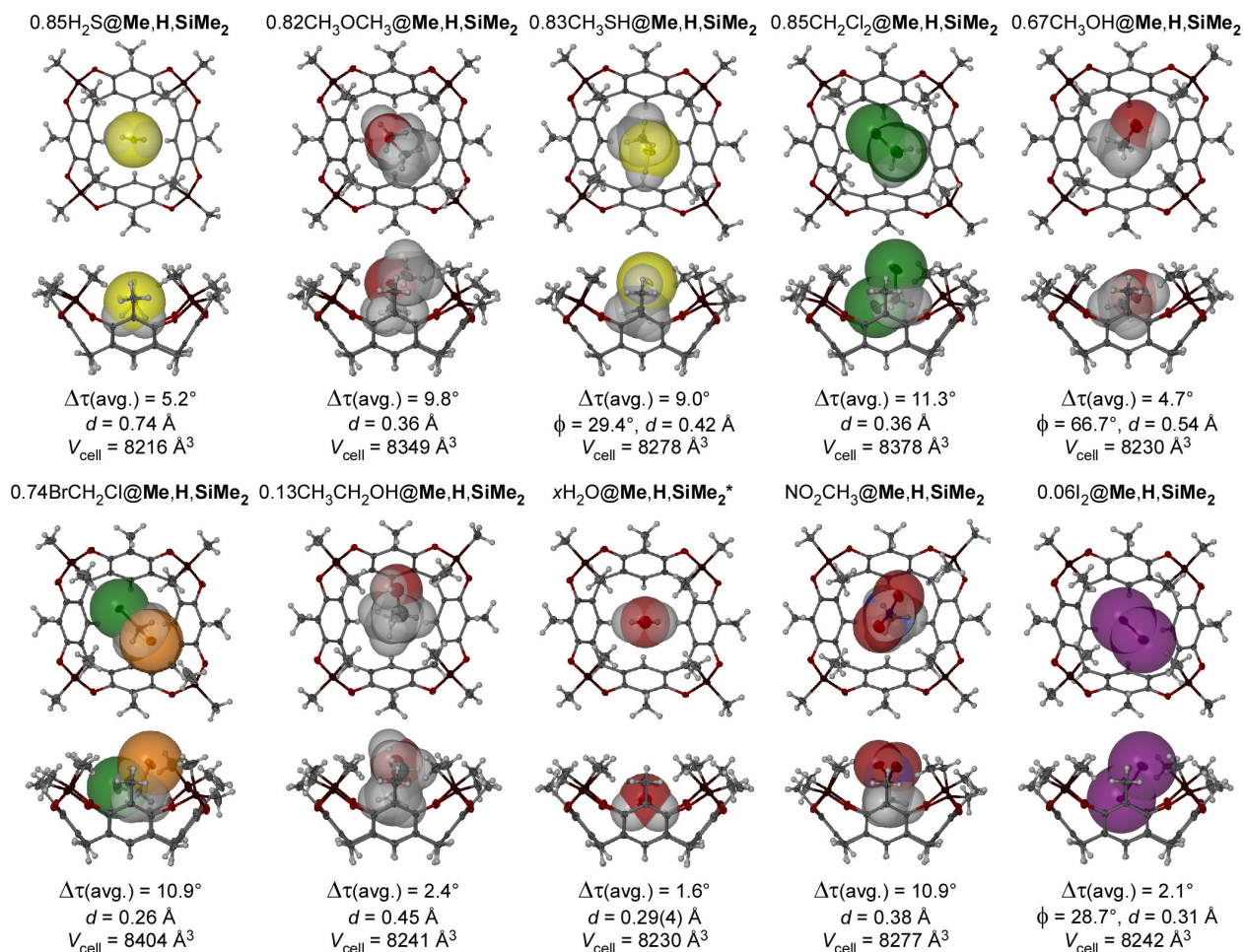


**Supporting Figure S66.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, w. TMS) of EtCl@**Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** batch crystals at Day 0. The integrated area of the signal at 3.55 ppm equates to 1.04 equivalents of chloroethane.



**Supporting Figure S67.** TGA [open pan] of EtCl@**Me<sub>2</sub>H<sub>2</sub>SiMe<sub>2</sub>** at Day 0 (black) and derivative weight curve (orange). The 7.6% mass loss equates to 0.98 equivalents of EtCl.

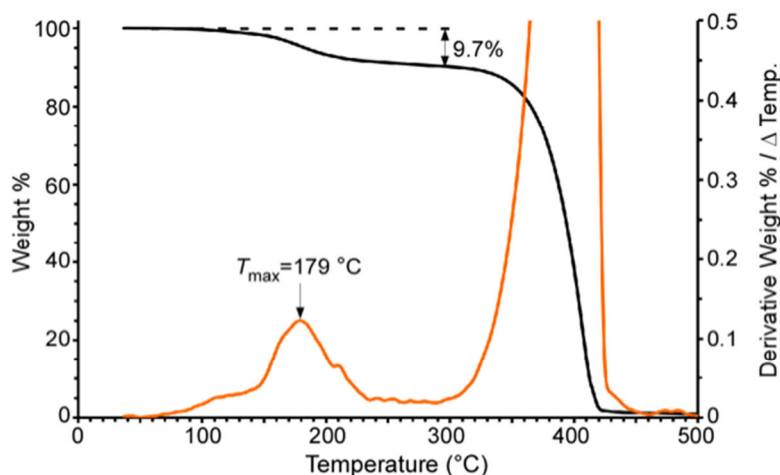




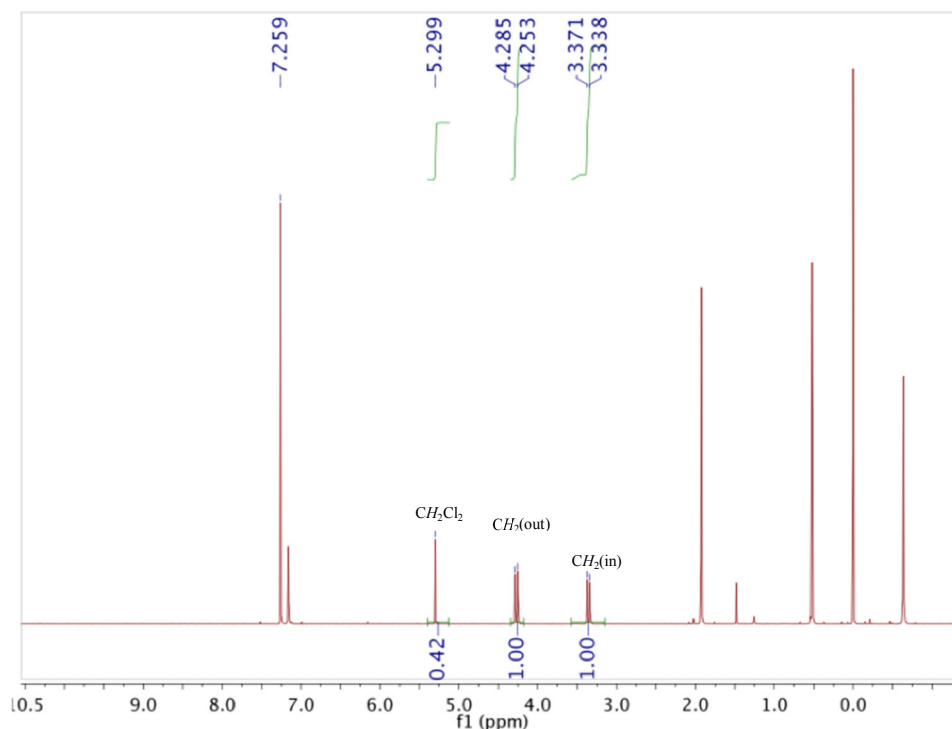
**Supporting Figure S68.** TEPs of isostructural  $x(\text{gas/solvent})@ \text{Me,H,SiMe}_2$  ( $x \leq 1$ ) clathrates (at 100 K - 50% probability level), along with summary structural parameters  $V_{\text{cell}}$ ,  $\Delta\tau(\text{avg.})$ ,  $\phi$ , and  $d$ , defined in the text. The esds of  $d$  for  $x(\text{H}_2\text{O})@ \text{Me,H,SiMe}_2$  was found from multiple hydrate crystal structures. The  $d$  for  $0.85(\text{H}_2\text{S})@ \text{Me,H,SiMe}_2$  was measured from the plane of all upper benzene carbons and the sulfur atom (not the hydrogens). Disordered bromochloromethanes are omitted for clarity. (Colors - gray - carbon, red - oxygen, maroon - silicon, white - hydrogen, green - chlorine, yellow - sulfur, purple - iodine, orange - bromine, blue - nitrogen).

***0.85(CH<sub>2</sub>Cl<sub>2</sub>)@Me,H,SiMe<sub>2</sub>***

**Me,H,SiMe<sub>2</sub>** was dissolved in dichloromethane and slow evaporation of the solvent yielded single crystals of (0.85)CH<sub>2</sub>Cl<sub>2</sub>@**Me,H,SiMe<sub>2</sub>** that were analyzed by SCXRD (Table S4). TGA data (Figure S69) shows a mass loss corresponding to 0.97 eq. CH<sub>2</sub>Cl<sub>2</sub> per cavitant. <sup>1</sup>H NMR (Figure S70) shows 0.84 eq. of CH<sub>2</sub>Cl<sub>2</sub> per cavitant.



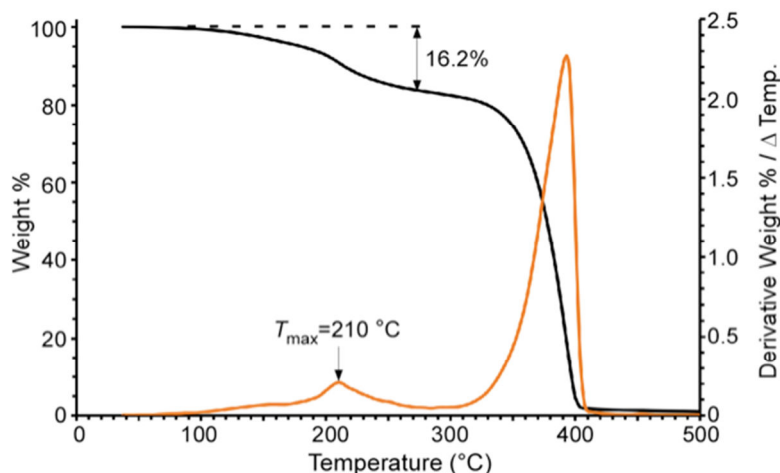
**Supporting Figure S69.** TGA [open pan] of CH<sub>2</sub>Cl<sub>2</sub>@**Me,H,SiMe<sub>2</sub>** at Day 0 (black) and derivative weight curve (orange). A 9.7% mass loss equates to 0.97 equivalents of CH<sub>2</sub>Cl<sub>2</sub>.



**Supporting Figure S70.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, w. TMS) of 0.85(CH<sub>2</sub>Cl<sub>2</sub>)@**Me,H,SiMe<sub>2</sub>** batch crystals at Day 0. The integrated signal at 5.3 ppm equates to 0.84 equivalents of dichloromethane.

### ***CH<sub>3</sub>I@Me<sub>4</sub>H<sub>4</sub>SiMe<sub>2</sub>***

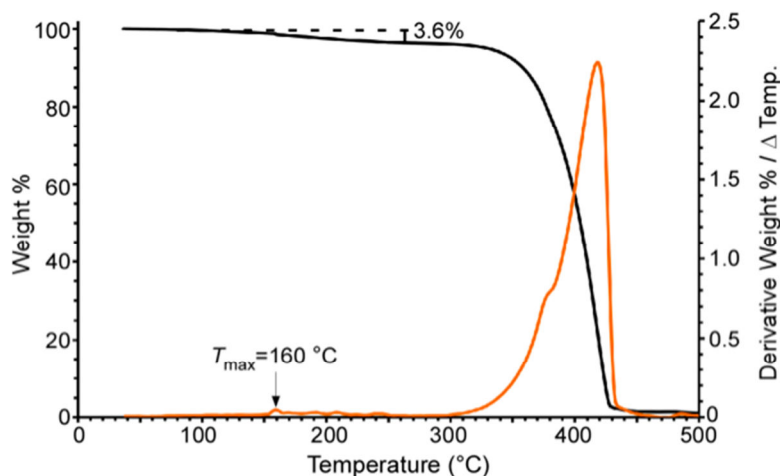
**Me<sub>4</sub>H<sub>4</sub>SiMe<sub>2</sub>** was dissolved in iodomethane and slow evaporation of the solvent yielded single crystals of **CH<sub>3</sub>I@Me<sub>4</sub>H<sub>4</sub>SiMe<sub>2</sub>** that were analyzed by SCXRD (Table S4). A thermal ellipsoid plot is shown in Figure 2 in the paper. TGA data (Figure S71) shows approximately 1.0 eq. of CH<sub>3</sub>I per cavitand.



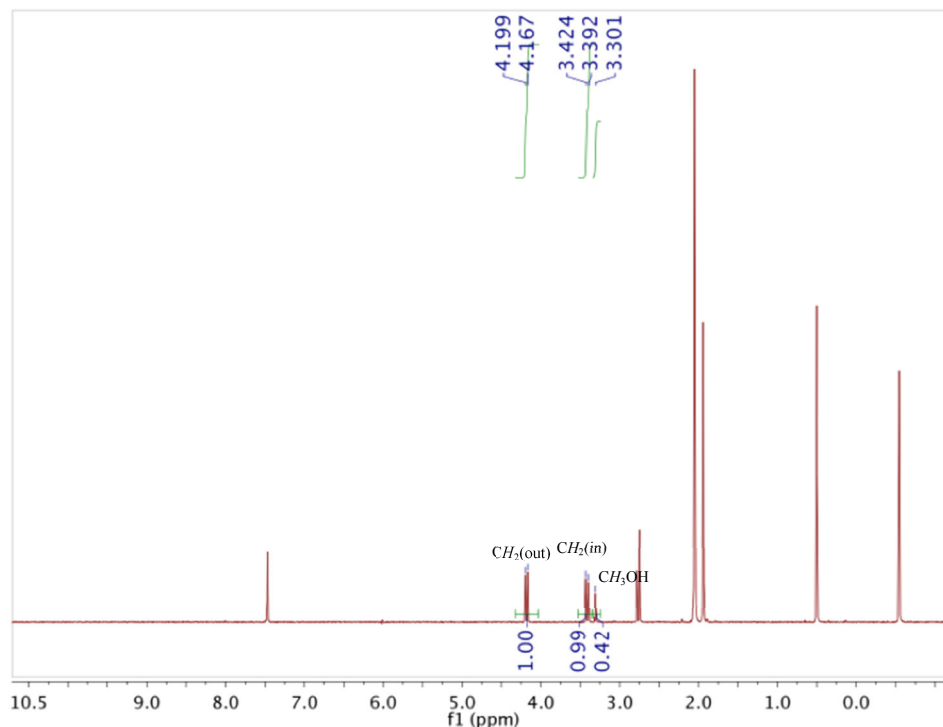
**Supporting Figure S71.** TGA [open pan] of **CH<sub>3</sub>I@Me<sub>4</sub>H<sub>4</sub>SiMe<sub>2</sub>** at Day 0 (black) and derivative weight curve (orange). A 16.2% mass loss equates to 1.05 equivalents of CH<sub>3</sub>I.

### ***0.67(CH<sub>3</sub>OH)@Me<sub>4</sub>H<sub>4</sub>SiMe<sub>2</sub>***

A saturated solution of **Me<sub>4</sub>H<sub>4</sub>SiMe<sub>2</sub>** in CHCl<sub>3</sub> (1 mL) was placed in a glass screw cap vial with 3 mL of MeOH and heated to re-dissolve any precipitate. Single crystals of **0.67(CH<sub>3</sub>OH)@Me<sub>4</sub>H<sub>4</sub>SiMe<sub>2</sub>** were isolated and analyzed by SCXRD (Table S4). TGA data (Figure S72) shows a mass loss of the bulk material corresponding to 0.90 eq. of CH<sub>3</sub>OH per cavitand. <sup>1</sup>H NMR (Figure S73) shows 0.56 eq. of CH<sub>3</sub>OH per cavitand.



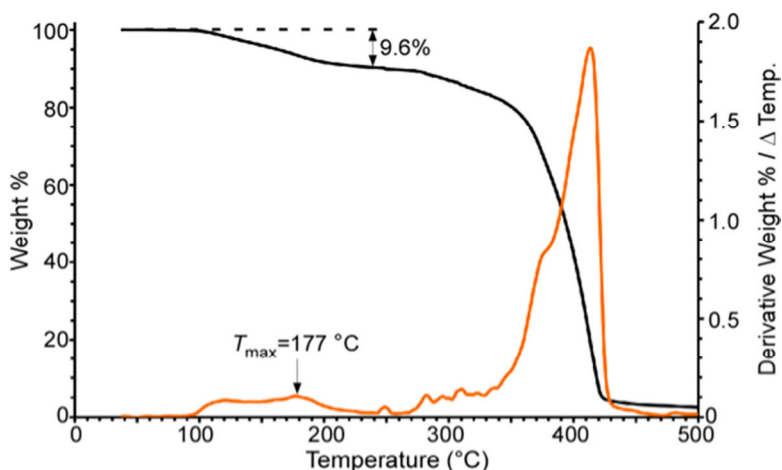
**Supporting Figure S72.** TGA [open pan] of **0.67(CH<sub>3</sub>OH)@Me<sub>4</sub>H<sub>4</sub>SiMe<sub>2</sub>** at Day 0 (black) and derivative weight curve (orange). A 3.6% mass loss equates to 0.90 equivalents of CH<sub>3</sub>OH.



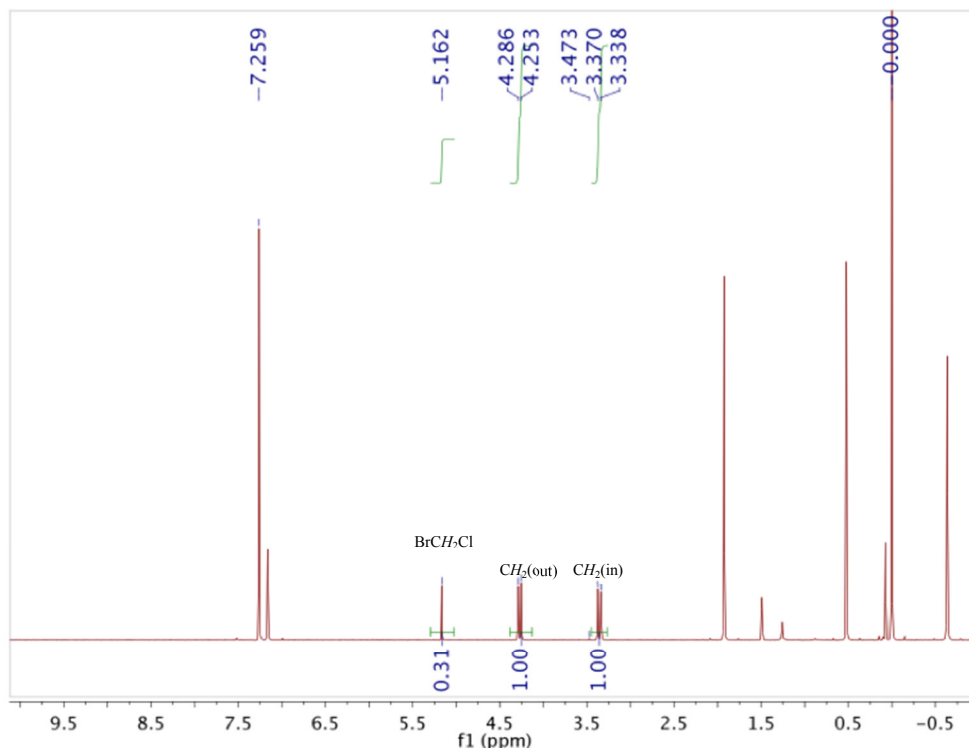
**Supporting Figure S73.**  $^1\text{H}$  NMR spectrum (acetone- $\delta_6$ ) of  $0.67(\text{CH}_3\text{OH})@\text{Me,H,SiMe}_2$  batch crystals at Day 0. The integrated area of the signal at 3.3 ppm equates to 0.56 equivalents of methanol.

**$0.74(\text{BrCH}_2\text{Cl})@\text{Me,H,SiMe}_2$**

$\text{Me,H,SiMe}_2$  was dissolved in bromochloromethane and slow evaporation of the solvent yielded single crystals of  $0.74(\text{BrCH}_2\text{Cl})@\text{Me,H,SiMe}_2$  that were analyzed by SCXRD (Table S4). TGA data (Figure S74) shows a mass loss corresponding to 0.63 eq. of  $\text{BrCH}_2\text{Cl}$  per cavitant.  $^1\text{H}$  NMR (Figure S75) shows 0.62 eq. of  $\text{BrCH}_2\text{Cl}$  per cavitant.



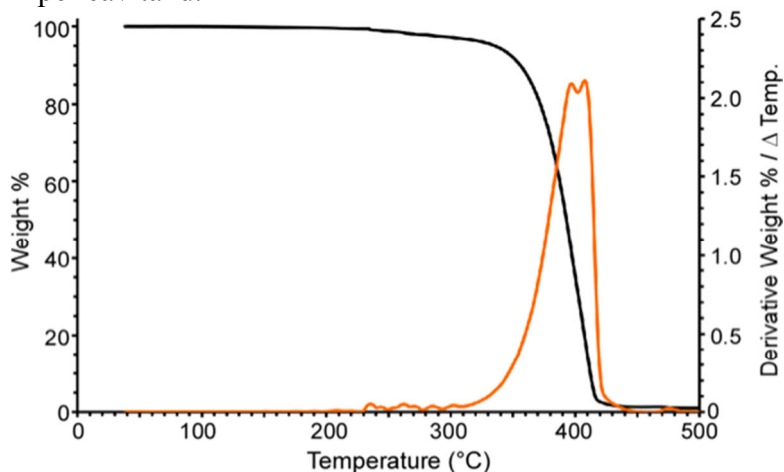
**Supporting Figure S74.** TGA [open pan] of  $0.74(\text{BrCH}_2\text{Cl})@\text{Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). The 9.6% mass loss equates to 0.63 equivalents of  $\text{ClCH}_2\text{Br}$ .



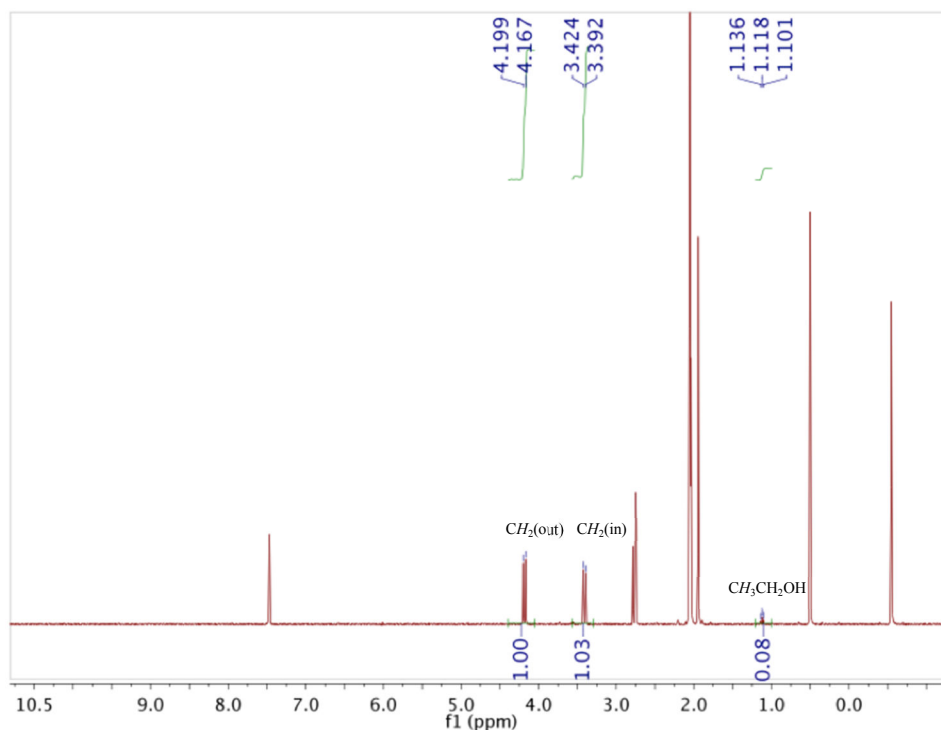
**Supporting Figure S75.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of  $0.74(\text{BrCH}_2\text{Cl})@\text{Me,H,SiMe}_2$  batch crystals at Day 0. The integrated area of the signal at 5.2 ppm equates to 0.62 equivalents of bromochloromethane.

#### ***0.13(EtOH)@Me,H,SiMe<sub>2</sub>***

A saturated solution of **Me,H,SiMe<sub>2</sub>** in  $\text{CHCl}_3$  (1 mL) was placed in a glass screw cap vial with 3 mL of EtOH and heated to re-dissolve any precipitate. Single crystals of **0.13(EtOH)@Me,H,SiMe<sub>2</sub>** were harvested after 1-2 days and analyzed by SCXRD (Table S4). TGA data (Figure S76) shows a mass loss corresponding to release of EtOH and sublimation occurring simultaneously.  $^1\text{H}$  NMR (Figure S77) shows 0.11 eq. of EtOH per cavitant.



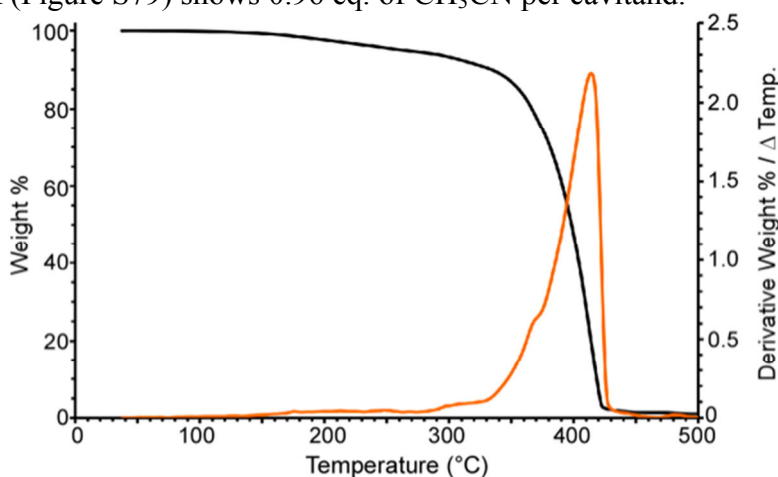
**Supporting Figure S76.** TGA [open pan] of **0.13(EtOH)@Me,H,SiMe<sub>2</sub>** at Day 0 (black) and derivative weight curve (orange). A weight loss % was not determined since there is no well-defined weight loss step separate from co-sublimation.



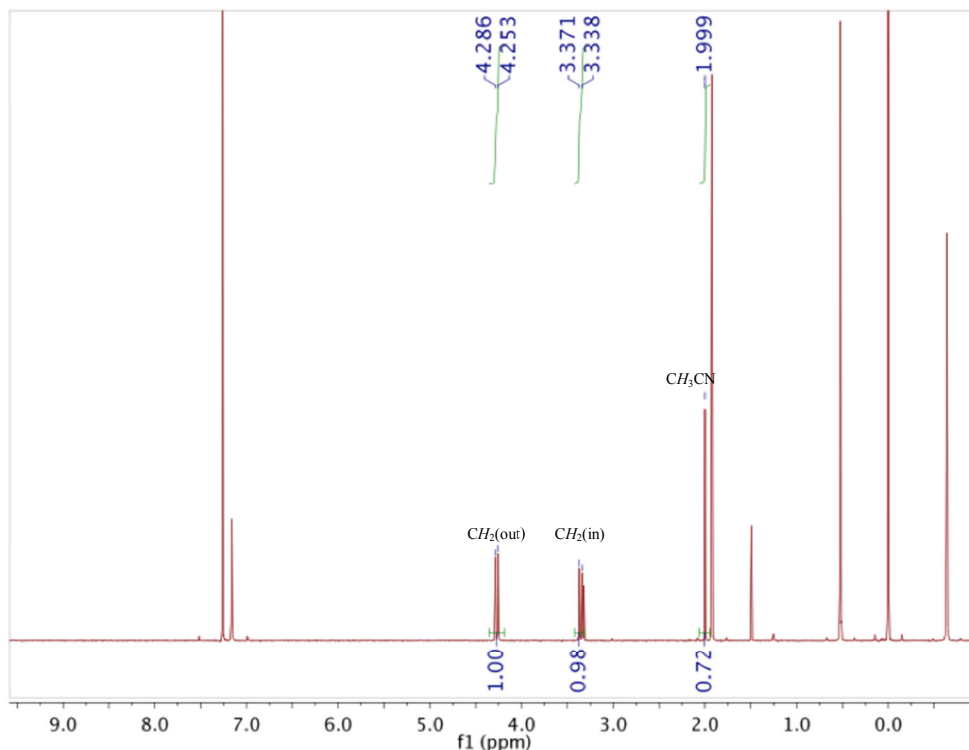
**Supporting Figure S77.**  $^1\text{H}$  NMR spectrum (acetone- $\delta_6$ ) of 0.13(EtOH)@Me,H,SiMe<sub>2</sub> batch crystals at Day 0. The integrated area of the signal at 1.12 ppm equates to 0.11 equivalents of ethanol.

### ***CH<sub>3</sub>CN@Me,H,SiMe<sub>2</sub>***

Me,H,SiMe<sub>2</sub> was dissolved in acetonitrile and slow evaporation of the solvent yielded single crystals of CH<sub>3</sub>CN@Me,H,SiMe<sub>2</sub> that were analyzed by SCXRD (Table S4). TGA data (Figure S78) shows that the mass loss corresponding to release of CH<sub>3</sub>CN could not be resolved from the mass loss by sublimation.  $^1\text{H}$  NMR (Figure S79) shows 0.96 eq. of CH<sub>3</sub>CN per cavitand.



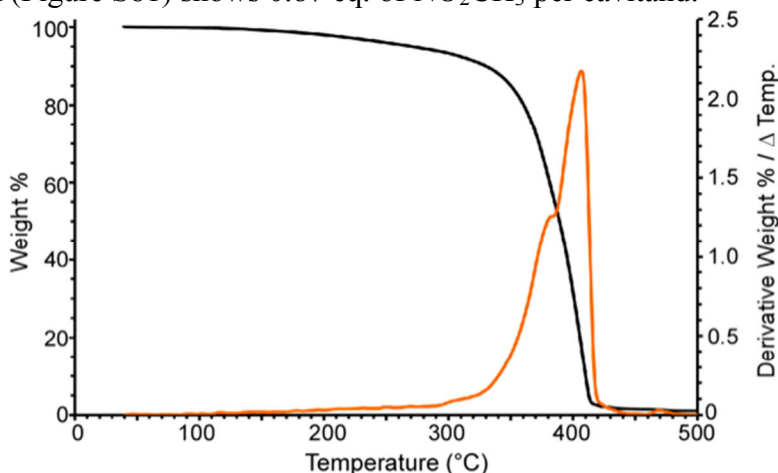
**Supporting Figure S78.** TGA [open pan] of CH<sub>3</sub>CN@Me,H,SiMe<sub>2</sub> at Day 0 (black) and derivative weight curve (orange). A weight loss % was not determined since there is no well-defined weight loss step separate from co-sublimation.



**Supporting Figure S79.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , w. TMS) of  $\text{CH}_3\text{CN}@\text{Me,H,SiMe}_2$  batch crystals at Day 0. The integrated area of the signal at 2.0 ppm equate to 0.96 equivalents of acetonitrile.

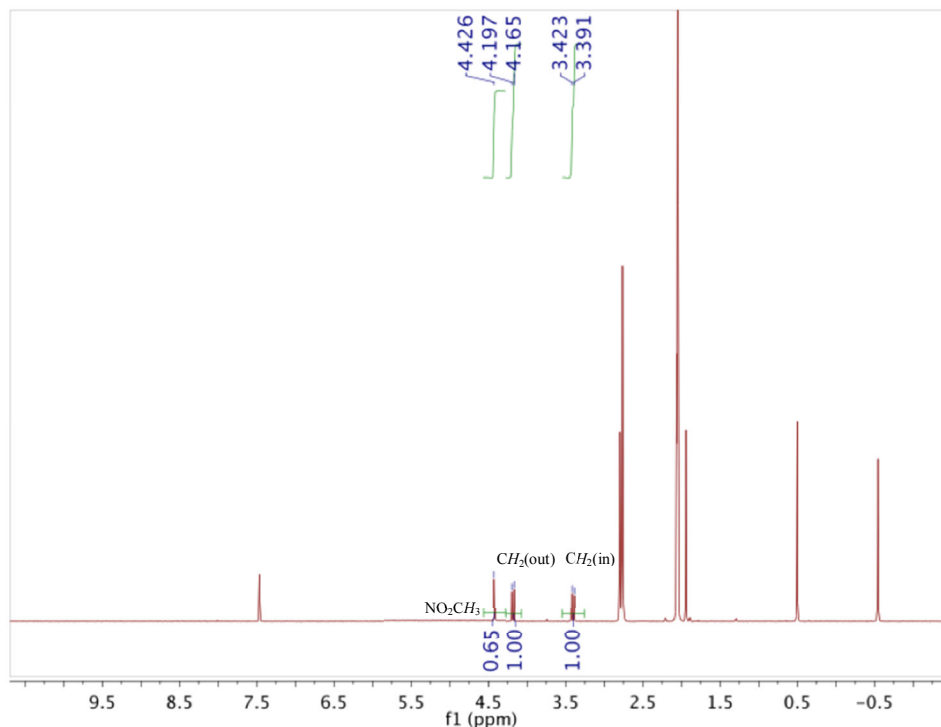
#### $\text{NO}_2\text{CH}_3@\text{Me,H,SiMe}_2$

$\text{Me,H,SiMe}_2$  was dissolved in nitromethane and slow evaporation of the solvent yielded single crystals of  $\text{NO}_2\text{CH}_3@\text{Me,H,SiMe}_2$  that were analyzed by SCXRD (Table S4). TGA data (Figure S80) shows that the mass loss corresponding to release of  $\text{NO}_2\text{CH}_3$  could not be resolved from the mass loss by sublimation.  $^1\text{H}$  NMR (Figure S81) shows 0.87 eq. of  $\text{NO}_2\text{CH}_3$  per cavitand.



**Supporting Figure S80.** TGA [open pan] of  $\text{NO}_2\text{CH}_3@\text{Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). A weight loss % was not determined since there is no well-defined weight loss step separate from co-sublimation.

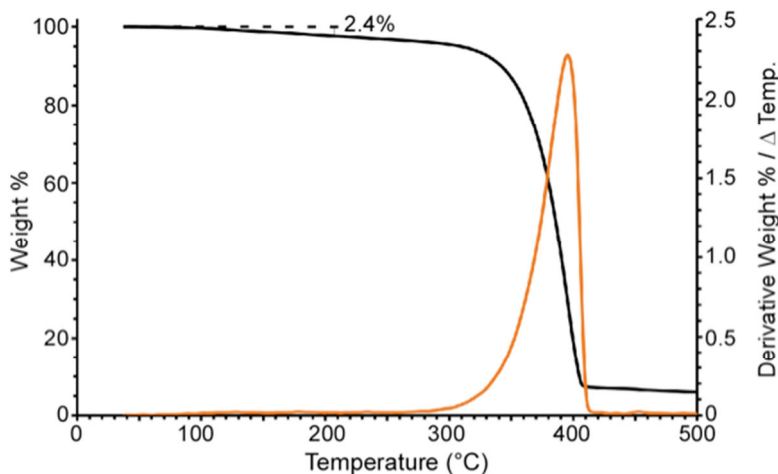




**Supporting Figure S81.**  $^1\text{H}$  NMR spectrum (acetone- $\delta_6$ ) of  $0.97(\text{NO}_2\text{CH}_3)@\text{Me,H,SiMe}_2$  batch crystals at Day 0. The integrated area of the signal at 4.45 ppm equate to 0.87 equivalents of nitromethane.

***0.06(I<sub>2</sub>)@Me,H,SiMe<sub>2</sub>***

Approximately 10 mg of  $\text{I}_2$  was added to a saturated solution of  $\text{Me,H,SiMe}_2$  in  $\text{CHCl}_3$  (1 mL) and slow evaporation of the solvent yielded single crystals of  $0.06(\text{I}_2)@\text{Me,H,SiMe}_2$  that were analyzed by SCXRD (Table S4). TGA data (Figure S82) shows a mass loss corresponding to 0.06 eq. of  $\text{I}_2$  per cavitant.



**Supporting Figure S82.** TGA [open pan] of  $0.06(\text{I}_2)@\text{Me,H,SiMe}_2$  at Day 0 (black) and derivative weight curve (orange). The 2.4% mass loss equates to 0.08 equivalents of  $\text{I}_2$ .



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