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Supplementary Material

The Elusive Ethenediselone, Se=C=C=Se

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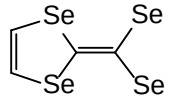
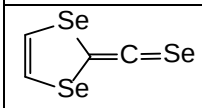
1. Further Computational Results

The IR spectra of the possible fragmentation products of **1** and **2** were calculated at the B3LYP/6-31++G(3df,2p) level. Only the key peaks with reasonably high intensities are reported in Table S1. It is seen that the calculated IR frequencies of CSe_2, C_2H_2 and CH_2=C=Se agree very well with the experimental values. For C_2Se_2 the strongest absorption is predicted to occur at 930 cm^{-1}, and this frequency is readily confirmed by MP2, CCSD and CASSCF calculations. A distinct absorption at 906 cm^{-1} in the IR spectrum from the FVP of the tetramethyl-derivative **2** may be ascribed to C_2Se_2. This peak was not observed in the FVP of **1**, where instead a very weak absorption at 784 cm^{-1} could possibly be due to the singlet 1,3-diselenolylidene with a predicted frequency of 785 cm^{-1}. CSe_2, HC≡CH, MeC≡CMe and H_2C=C=Se are clearly observed in the mass and IR spectra as described in Sections 1 and 2.

Table S1. Calculated vibrational frequencies (cm^{-1}) and infrared intensities (km mol^{-1}) of C_2Se_2 and fragmentation products of tetraselenafulvalenes **1** and **2**.[A]

Species	frequency[B] (cm^{-1})	infrared intensity (km mol^{-1})	observed frequency (cm^{-1})
SeCCSe ($^3\Sigma_g^-$)	930.0	57.1	906
SeCCSe ($^1\Delta_g$)	930.3	51.9	
SeCCSe ($^1\Sigma_g^+$)	932.4	51.9	
CSe_2	1284.1	550.2	1298
CSe	1029.7	53.1	1036/1022[C]
HC≡CH	740.3	99.7	735
	3295.6	90.8	3298
MeC≡CMe	1030.0	0.6	1036/1022[C]
	1433.7	14.4	1447
	2919.0	66.9	2936
	2970.1	20.5	2976
CH_2=C=Se	655.1	9.7	[D]
	871.9	69.6	869
	1708.0	351.8	1699
	3222.1	23.1	
CMe_2=C=Se	1109.3	87.6	
	1365.9	26.0	
	1433.8	10.7	
	1442.0	15.6	
	1748.9	209.5	[E]
	2907.9	17.4	
	2910.5	78.9	
	2952.9	38.2	
	3013.3	12.0	
1,3-diselenole carbene	665.7	66.1	[D]
(**4**)	784.7	22.0	784
4,5-dimethyl-1,3-diselenole carbene	773.0	16.1	
	1126.7	10.1	
	1437.9	15.5	
	2924.1	20.9	
	2925.8	32.3	
	2971.2	18.4	
Selenirene	587.6	74.5	
	872.0	60.1	
	1683.2	29.3	

	3160.0	25.0	
C_2Se_4 (**6**)	799.5	155.7	
	978.9	22.8	
	1084.2	8.6	
 (**3**)	650.8	17.1	
	656.0	42.6	
	814.9	93.8	
	908.0	11.0	
	1139.9	87.9	
	1469.9	18.2	
 (**5**)	600.7	58.6	
	695.9	29.8	
	800.2	39.1	
	1541.6	47.2	
	1709.0	154.3	

[A] B3LYP/6-311++G(3df,2p) level.

[B] Scaled by a factor of 0.967: M. W. Wong, *Chem. Phys. Lett.* **1996**, *256*, 391.

Precomputed vibrational scaling factors from the Computational Chemistry Comparison and Benchmark Database (CCCBC) in National Institute of Standards and Technology (NIST), web link: http://cccbdb.nist.gov/vibscalejust.asp (accessed 10 February, 2014).

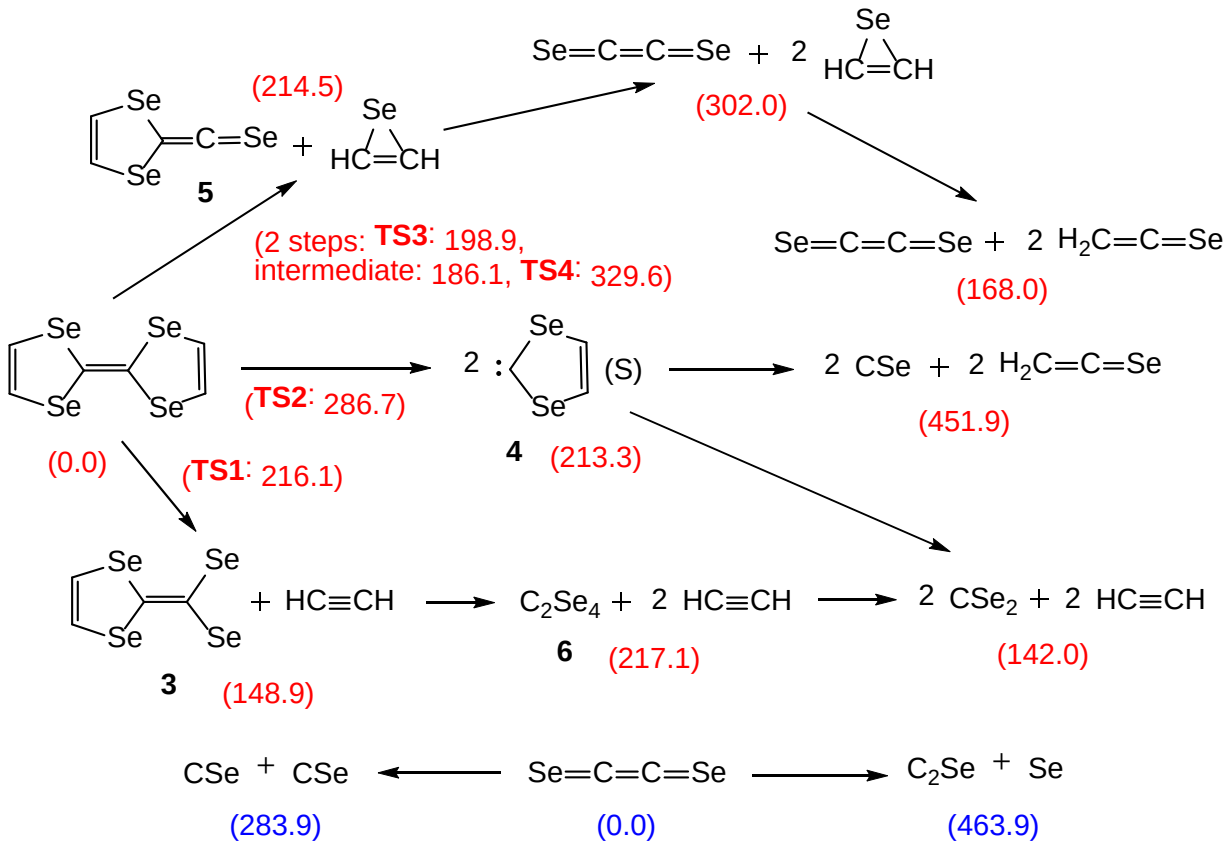
[C] See text in paper proper.

[D] Outside recorded spectral range.

[E] Weak peaks in the 1700 cm^{-1} range could be due to this compound.

2. Calculated reaction free energies at 298 K

The reaction free energies at room temperature (298 K) for the various possible fragmentation pathways of **1** at the B3LYP/6-311++G(3df,2p) level are summarized in Scheme S1. Compared to the reaction free energies at 900 °C (Scheme 2 in main text), the calculated fragmentation energies are substantially more endothermic due to the entropy (tempertaure) effect. However, the changes in activation barriers are small. Overall, the fragmentation of **1** to CSe_2 + C_2H_2 remains the most favourable pathway both kinetically and thermodynamically. Both C=C bond cleavage and dissociation of **1** to C_2Se_2 + selenirene are less favorable fragmentation pathways with significantly larger activation barriers. The optimzed geometries of selected intermediates (**3** – **6**) and transition states (**TS1** – **TS4**) are given in Fig. S1.



Scheme S1. Fragmentation pathways of tetraselenafulvalene **1** and C_2Se_2. Calculated relative free energies (ΔG_{298}, kJ mol^{-1}) at the B3LYP/6-311++G(3df,2p) level are given in parentheses.

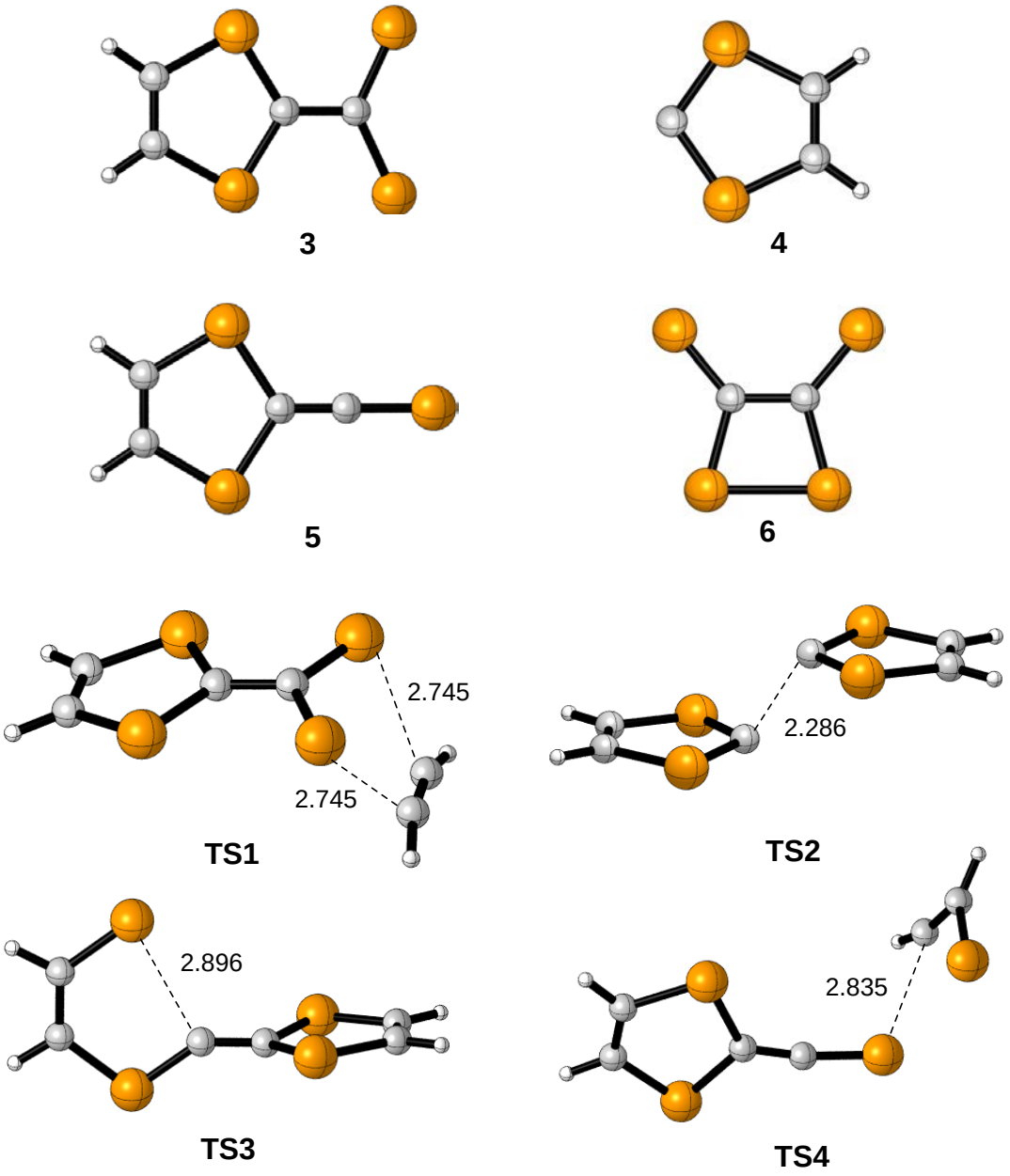


Fig. S1. Optimized (B3LYP/6-311++G(3df,2p) geometries of selected intermediates and transition states.

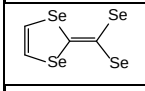
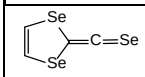
3. Computational Details

Table S2. Cartesian coordinates and total energies (E, Hartrees) of the B3LYP/6-311++G(3df,2p) optimized geometries of all calculated structures. The number of imaginary frequencies is given in parenthesis.

C_2Se_2 ($^3\Sigma_g^-$) E = -4879.250243 (0)			
C	0.000000	0.000000	0.630860
C	0.000000	0.000000	-0.630860
Se	0.000000	0.000000	2.354269
Se	0.000000	0.000000	-2.354269
C_2Se_2 ($^1\Delta_g$) E = -4879.266835 (0)			
C	0.631111	0.000000	0.000000
C	-0.631111	0.000000	0.000000
Se	2.354647	0.000000	0.000000
Se	-2.354647	0.000000	0.000000
C_2Se_2 ($^1\Sigma_g^+$) E = -4879.271897 (0)			
C	0.000000	0.000000	0.632392
C	0.000000	0.000000	-0.632392
Se	0.000000	0.000000	2.355052
Se	0.000000	0.000000	-2.355052
CSe E = -2439.571674 (0)			
C	0.000000	0.000000	0.001499
Se	0.000000	0.000000	1.678501
CSe2 E = -4841.213070 (0)			
C	0.000000	0.000000	0.000000
Se	0.000000	0.000000	1.696382
Se	0.000000	0.000000	-1.696382
C_2H_2 E = -77.362009 (0)			
H	0.000000	0.000000	-1.660295
C	0.000000	0.000000	-0.598106
H	0.000000	0.000000	1.660295
C	0.000000	0.000000	0.598106
MeC≡CMe E = -156.037771 (0)			
C	0.000000	0.000000	0.600470

tetraselenofulvalene **1** E = -9837.263755 (0)			
Se	-1.728383	1.602281	-0.057990
C	-3.327584	0.664667	0.346351
C	-3.328109	-0.663426	0.346104
Se	-1.729651	-1.602155	-0.058588
C	-0.670667	-0.000357	-0.050113
H	-4.200816	1.268519	0.546891
H	-4.201818	-1.266662	0.546420
C	0.668140	-0.000887	-0.049044
Se	1.725870	-1.603520	-0.055837
Se	1.727137	1.600912	-0.055238
C	3.324941	0.662035	0.351697
H	4.198325	1.265194	0.553655
C	3.324416	-0.666059	0.351449
H	4.197325	-1.269982	0.553178
1,3-dithiole carbene (**4**) E = -4918.580221 (0)			
C	0.000000	0.000000	-2.135896
Se	-1.492920	0.000000	-1.083857
C	-0.667917	0.000000	0.633186
C	0.667917	0.000000	0.633186
Se	1.492920	0.000000	-1.083857
H	-1.287829	0.000000	1.518619
H	1.287829	0.000000	1.518619
4,5-dimethyl-1,3-diselenole carbene E = -4997.240154 (0)			
C	0.000125	0.370201	-2.106499
Se	-1.483626	0.247637	-1.055717
C	-0.670964	0.045065	0.681778
C	0.670995	0.045096	0.681835
Se	1.483794	0.247705	-1.055591

C	0.000000	0.000000	-0.600470
C	0.000000	0.000000	2.057124
H	0.479926	0.897443	2.451960
H	0.537245	-0.864349	2.451960
H	-1.017171	-0.033093	2.451960
C	0.000000	0.000000	-2.057124
H	0.537245	0.864349	-2.451960
H	-1.017171	0.033093	-2.451960
H	0.479926	-0.897443	-2.451960
CH_2=C=Se E = -2478.939987 (0)			
C	0.000000	0.000000	0.957862
C	0.000000	0.000000	2.259620
H	0.928803	0.000000	2.816992
H	-0.928803	0.000000	2.816992
Se	0.000000	0.000000	-0.744586
CMe_2=C=Se E = -2557.600840 (0)			
C	0.000000	0.000000	0.175963
C	0.000000	0.000000	1.480243
Se	0.000000	0.000000	-1.534738
C	1.293290	0.000000	2.263117
H	1.344347	0.881775	2.907164
H	2.164321	0.000000	1.612027
H	1.344347	-0.881775	2.907164
C	-1.293290	0.000000	2.263117
H	-1.344347	0.881775	2.907164
H	-1.344347	-0.881775	2.907164
H	-2.164321	0.000000	1.612027
TS1 E = -9837.185706 (1)			
Se	1.873805	0.034509	1.608014
C	3.478804	0.381352	0.664340
C	3.479810	0.374285	-0.664053
Se	1.876280	0.017307	-1.606460
C	0.859278	-0.288875	0.001702
H	4.352506	0.588320	1.266153
H	4.354416	0.574894	-1.266703
C	-0.440873	-0.484889	0.001825
Se	-1.688789	-1.716973	0.007418
C	-1.589806	-0.092465	1.861263
H	-2.237342	-0.965070	1.757870
H	-1.034812	-0.201213	2.791946
H	-2.237022	0.780729	1.961674
C	1.589743	-0.092390	1.861397
H	2.236885	0.780850	1.961884
H	1.034676	-0.201201	2.792029
H	2.237354	-0.964945	1.758043
C_2Se E = -2477.587065 (0)			
C	0.000000	0.000000	0.648274
C	0.000000	0.000000	-0.653567
Se	0.000000	0.000000	2.366517
TS3 E = -9837.148878 (1)			
Se	-0.240201	1.899264	-1.462412
C	0.186925	3.563284	-0.646518
C	0.274922	3.563055	0.684582
Se	-0.041117	1.898746	1.549034
C	-0.273364	0.829663	0.051900
C	1.296039	-0.829632	-0.052133
Se	1.262882	-1.899220	1.462188
Se	1.063788	-1.898727	-1.549257
C	0.747753	-3.563030	-0.684790
C	0.835756	-3.563247	0.646310
H	0.336058	4.429052	-1.276385
H	0.505696	4.428611	1.289632
H	0.686625	-4.429010	1.276185
H	0.516979	-4.428591	-1.289832
TS2 E = -9837.127621 (1)			
Se	-1.214777	-1.614129	0.040582
C	-3.095455	-1.688850	0.262198
C	-3.822976	-0.581466	0.172806
Se	-2.985661	1.080950	-0.182390
C	-1.220122	0.299414	-0.249282
H	-3.512587	-2.666888	0.457163
H	-4.897274	-0.556619	0.289433
C	-0.142186	0.998888	-0.476335
Se	1.416205	1.655539	-0.734262

Se	-2.211430	1.807027	-0.009446
C	-3.504676	0.511892	-0.003954
H	-4.538781	0.844160	-0.005765
C	-3.321632	-0.840950	0.002279
H	-4.142318	-1.546021	0.005138
TS4 E = -9837.176392 (1)			
Se	-1.579153	1.581263	0.335870
C	-3.105278	0.666428	0.969385
C	-3.106349	-0.668757	0.967491
Se	-1.581694	-1.584239	0.331380
C	-0.621284	-0.001839	0.038129
H	-3.936124	1.273391	1.301664
H	-3.938170	-1.275325	1.298049
C	0.717968	-0.002302	-0.392645
Se	1.579166	-1.624232	-0.582241
Se	1.581770	1.618773	-0.577636
C	3.364625	0.602881	1.245825
H	3.587345	1.615848	1.475419
C	3.363640	-0.616402	1.244092
H	3.584739	-1.630371	1.470813
C_2Se_4 (**6**) E = -9682.413439 (0)			
Se	-0.094969	1.119827	-1.639547
Se	-0.142526	1.703530	1.571577
C	0.222803	0.675321	0.178753
C	0.820965	-0.675994	0.135636
Se	1.368607	-1.710285	1.462650
Se	0.893089	-1.112304	-1.710769
Se	3.994570	-0.124065	-0.963132
C	4.199982	-0.003697	0.949275
H	4.980046	-0.477351	1.531806
C	3.208829	0.733388	1.258567
H	2.528639	1.270123	1.876868
 (**3**) E = -9759.824361 (0)			
Se	-1.583962	1.577319	0.093443
C	-3.210461	0.670778	0.392593
C	-3.210583	-0.668761	0.392876
Se	-1.584249	-1.575724	0.094107
C	-0.622052	0.000673	-0.083064
H	-4.090991	1.277939	0.554330
H	-4.091223	-1.275693	0.554868
C	0.799827	0.000488	-0.344427
Se	1.569862	-1.664189	-0.485647
Se	1.570165	1.664965	-0.486349
 (**5**) E = -7358.256340 (0)			
Se	-0.480485	-2.212189	-0.285342
C	-2.357395	-2.393547	-0.502166
C	-3.142955	-1.325645	-0.472906
Se	-2.404737	0.403669	-0.213670
C	-0.601658	-0.289841	-0.096418
H	-2.717963	-3.402446	-0.646018
H	-4.216869	-1.364810	-0.590189
C	0.436694	0.468802	0.092604
Se	1.800837	1.465475	0.340934
selenirene E = -2478.898669 (0)			
Se	-0.189381	-0.274212	1.759079
C	-0.632929	0.441364	-0.062892
C	0.627178	0.406096	0.056500
H	-1.521268	0.655746	-0.626796
H	1.616051	0.567938	-0.329543